Landfill Leachate Sorption Potential of Kate Valley Soils

A thesis submitted in part fulfilment of the requirements for the Degree of Masters of Engineering in Civil Engineering at the University of Canterbury

by

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Abstract

Kate Valley is a municipal waste landfill situated in Waipara, Northern Canterbury. It is a joint venture between the 6 local regional councils and Transwaste Canterbury Ltd to help dispose of waste quantities generated in the wider Canterbury region. Landfill waste disposal also generates waste streams. Major waste streams can include methane gas production and liquid leachate. One practice which can turn liquid leachate waste streams into a nutrient source for plants is land irrigation. It is important to have a thorough understanding of the interactions involved with leachate, soil structure, soil microbiology, flora. This thesis investigates the sorption mechanisms between Kate Valley soil and leachates, through batch and column experiments.

Sorption mechanisms between leachate and soil were investigated through batch and column tests. Ex-situ soil samples were extracted from Kate Valley, along with raw leachate samples for batch tests at a soil to liquid ratio of 30 g vs. 70 ml respectively. Tested dilution leachate strengths ranged from raw to 50x raw leachate dilution; meanwhile soil samples were categorized into 3 groups based on soil depth: 0-20 cm, 20-40 cm, and 40-60 cm.

Column tests were conducted on 3 extracted in-situ soil column monoliths. Column test irrigation conditions included: control case, 2x and 10x raw leachate dilution, and 200 mg/L KBr (bromide column), where the same soil column was used for bromine testing after control testing had ceased.

Batch results suggest deeper soils are less effective at sorption of ammonia, where partitioning coefficient ranged from $9.5x*10^{-7}$ to $6.4*10^{-7}$ L/mg for 0-20 cm soil to 40-60 cm soil respectively. Column results generally showed lower partitioning capacity than batch results, at $4*10^{-8}$ and $5*10^{-8}$ L/mg for 10x and 2x dilution leachate irrigation respectively.

Discrepancies in experimental data have been attributed to: different dilution leachates tested between batch and column tests, making it difficult for direct comparison; extreme soil to liquid ratios employed in experiments; direct data comparison between the “full-contact” experimental data (between leachate and soil), obtained from batch tests with column results, where not all soil may have been fully exposed for shrinkage of boundary layers of soil particles; and oxygen exposure of samples during testing and sampling, possibly encouraging nitrification.

Acknowledgements

I would like to thank the following people, without whom this study would not have been possible:

Dr. Mark Milke for his affable attitude, thesis guidance and patience.

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Transwaste Canterbury Ltd. and the team at Kate Valley Landfill.

Glossary

ANZECC – Australian and New Zealand Environment Conservation Council.

BOD/COD – Ratio of biochemical oxygen demand to chemical oxygen demand.

BOD_5/COD – ratio of 5-day biochemical oxygen demand to chemical oxygen demand.

BTC – Breakthrough curve.

CEC – cation exchange capacity.

Cliflo – NIWA's atmospheric activity reporting software.

Drainage – liquid which has drained from soil columns.

ECe – electrical conductivity.

Footprint – landfill footprint, area in which the landfill takes up.

MSL - Mean Sea level

NIWA – National institute water association.

NZWWA – New Zealand Water and Waste Association.

PV – Pore volume(s).

SAR – Sodium adsorption ratio.

SPSS – Statistical Package for the Social Sciences.

TDS – total dissolved solids

TKN – total Kjeldahl nitrogen.

TOC – Total organic carbon.

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SOIL ANALYSIS RESULTS (0-20CM DEPTH SOIL PRE-COLUMN TEST)

Hill Laboratories
BETTER TESTING BETTER RESULTS
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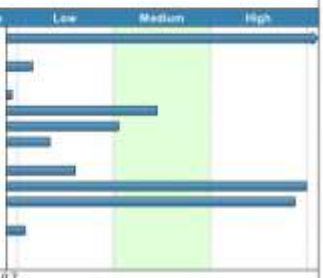
ANALYSIS REPORT

Client:	K Chu	**Lab No:**	1157187
Address:	C/- Department of Civil Engineering	**Date Registered:**	18-Jul-2013
	University of Canterbury	**Date Reported:**	24-Jul-2013
	Private Bag 4800	**Quote No:**	54087
	CHRISTCHURCH 8140	**Order No:**	534094
		Client Reference:	
		Submitted By:	K Chu

Sample Name: KCS001 **Lab Number:** 1157187.1
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range
pH	pH Units	8.0	5.8 - 6.3
Olsen Phosphorus	mg/L	7	20 - 30
Potassium	me/100g	0.12	0.50 - 0.80
Calcium	me/100g	8.7	6.0 - 12.0
Magnesium	me/100g	1.09	1.00 - 3.00
Sodium	me/100g	0.07	0.20 - 0.50
CEC	me/100g	10	12 - 25
Total Base Saturation	%	100	50 - 85
Volume Weight	g/mL	1.22	0.60 - 1.00
Organic Matter*	%	0.5	7.0 - 17.0
Total Carbon	%	0.3	
Total Nitrogen	%	< 0.04	0.30 - 0.60
Base Saturation %		K 1.3 Ca 87	Mg 10.9 Na 0.7
MAF Units		K 5 Ca 13	Mg 30 Na 4



The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information.
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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

SOIL ANALYSIS RESULTS (20-40CM DEPTH SOIL PRE-COLUMN TEST)

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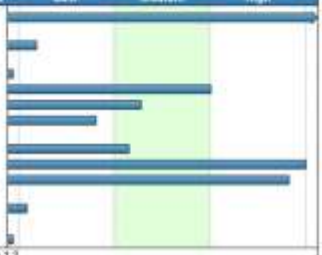
ANALYSIS REPORT Page 2 of 5

Client:	K Chu	**Lab No:**	1157187
Address:	C/- Department of Civil Engineering University of Canterbury Private Bag 4800 CHRISTCHURCH 8140	**Date Registered:**	18-Jul-2013
		Date Reported:	24-Jul-2013
		Quote No:	54087
		Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

Sample Name: KCS002 **Lab Number:** 1157187.2
Sample Type: SOIL General, Outdoor (S10)

Analyte		Level Found	Medium Range
pH	pH Units	8.3	5.8 - 6.3
Olsen Phosphorus	mg/L	8	20 - 30
Potassium	me/100g	0.13	0.50 - 0.80
Calcium	me/100g	12.1	6.0 - 12.0
Magnesium	me/100g	1.39	1.00 - 3.00
Sodium	me/100g	0.16	0.20 - 0.50
CEC	me/100g	14	12 - 25
Total Base Saturation	%	100	50 - 85
Volume Weight	g/mL	1.21	0.80 - 1.00
Organic Matter*	%	0.6	7.0 - 17.0
Total Carbon	%	0.3	
Total Nitrogen	%	0.04	0.30 - 0.60
Base Saturation %		K 0.9 Ca 87 Mg 11.2 Na 1.2	
MAF Units		K 3 Ca 18 Mg 42 Na 9	



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1. Introduction

Kate Valley landfill is an sanitary municipal waste landfill, a joint venture between the 6 local regional councils of Canterbury and Transwaste Canterbury Ltd; assisting the Burwood landfill with the great annual waste quantities generated in the Canterbury region.

All landfills produce waste streams (gas, leachate) which need to be addressed and managed to avoid polluting the environment and surrounding natural resources. This study will analyse leachate management for Kate Valley, where current leachate disposal method in practice is storage in detention tanks, periodically trucked back into Christchurch for disposal at the Bromley wastewater treatment plant. This method was viable as a method of leachate disposal during the early stages of landfill operation, however, leachate quantities have increased and current disposal methods are becoming less economically viable.

Landfill leachates need to be properly treated before disposal due to their high liquid pollutant concentrations, toxic to the environment. These contaminants can include heavy metals, organic content, nitrogen, salinity and very acidic pH for early leachates, especially those landfills still in their methanogenic phase. Methods of landfill leachate treatment have included dilution, biofiltering, and coagulation processes, to name a few.

More and more sanitary landfills have started to apply their collected landfill leachates to forested plantations (Smesrud, Duvendack, Obereiner, Jordahl, and Madison 2012; N. W. Macdonald, Rediske, Scull, and Wierzbicki 2008), effectively turning this waste stream into a fertiliser with potential beneficial effects to the growth of plantations. However, there are a large amount of chemical, physical and environmental factors which need to be assessed and management practices considered before successful implementation of landfill leachate irrigation. These factors may ultimately render landfill leachate irrigation unviable as a method of leachate disposal (from an economic standpoint), thus it is important to thoroughly investigate and research towards an understanding of the landfill leachate, soil sorption capacities, resiliency of plantations to leachate irrigation, and their interactive response to preserve the local environment.

The aim of this study is to conduct an in-depth analysis of the soil response to irrigation of landfill leachate; this specifically excludes any flora interactions and microbiological interactions involved. The experimental scope of this study includes thorough testing and characterisation of Kate valley leachate and soil. Their interactions will be investigated

through batch tests, and eventually soil and leachate sorption analysis in scaled in-situ soil monoliths (column test).

The aim of this study includes the analysis of literature for current landfill leachate irrigation practices to land, examining the various mechanisms and factors which contribute towards their successes and failures, as well as lessons learnt. These reviews will then be used to interpret analyse results of batch test and in-situ soil monolith experiments between Kate Valley soil and leachate; over various raw leachate dilution strengths and soil samples (vary by depth). This should provide an understanding of the sorption mechanisms involved with Kate Valley leachates and soils; to make informed decisions on the future prospect of leachate irrigation to land for Kate Valley.

1.1. Research overview

This Master's thesis research paper investigates the response of Kate Valley soil to the application of landfill leachate. Literature review has been conducted to gain an understanding of current practices of landfill leachate application to land around the world, and identify key elements that contribute towards their outcomes. Research will also be conducted into the various guidelines in which these leachate application projects use or develop to prevent contamination of resources, adhere to regulatory guidelines, and best management practice.

Laboratory experiments will consist of two major parts:

1) Batch test experiments will involve samples of ex-situ Kate Valley soil at various depths, mixed with landfill leachate of various concentrations. Following a sorption period, liquid samples are tested for contaminant concentrations to gain an understanding of the soil's sorption potential at various leachate concentrations.

2) Scaled column experiments will be conducted on excavated in-situ soil monolith columns. Landfill leachate will be irrigated at various concentrations upon these columns to analyse contaminant concentrations in drainage; which are subsequently used to plot breakthrough curve (BTC) for the contaminant.

Other miscellaneous laboratory tests will be conducted to gain further understanding of the materials, e.g. porosity, volatile solids, particle size distribution. Other tests which were not accessible for the student to conduct have been completed externally by Hills Laboratory.

This Master's thesis will investigate the adsorption behaviour of key contaminants with batch and column tests, by analysis of adsorption characteristics such as partitioning coefficient, contaminant breakthrough curves, and their effects in the specific case of Kate Valley soil and leachate.

1.2. Kate Valley site description

Figure 1. Kate valley landfill site in the South Island (Transwaste Canterbury, 2001).

Kate Valley landfill is located in the Waipara region of the Hurunui district, on the South Island of New Zealand, Figure 1. Its geological background consists of low permeability strata which forms the coastal hills of North Canterbury, predominantly formed in a marine environment from low-permeability deposits of compacted fine sands, silts and limestone. Local tectonic movements of South Island's geologic structure have uplifted these fine-grained deposits and folded them into the coastal hills that exist today.

Transwaste Canterbury (2002) has conducted extensive geological survey and soil bore results, revealing the 3 main geologic units in the area; these are: the Greenwood formation, Tokama siltstone and the Waikari formation, as shown in Figure 2 and Figure 3.

Greenwood formation consists of hard-silts and tightly packed fine to medium-sands, with partially cemented, discontinuous shells and conglomerate layers. The Greenwood layer

generally outcrops in the southern region of the landfill site and extends to depths of around 80m below ground.

Tokama siltstone consists of hard, slightly calcareous silty-fine sands and fine sandy-silts. It outcrops in the northern half of the landfill site, where it extends to depths of around 100m below ground, continuing below the Greenwood formation.

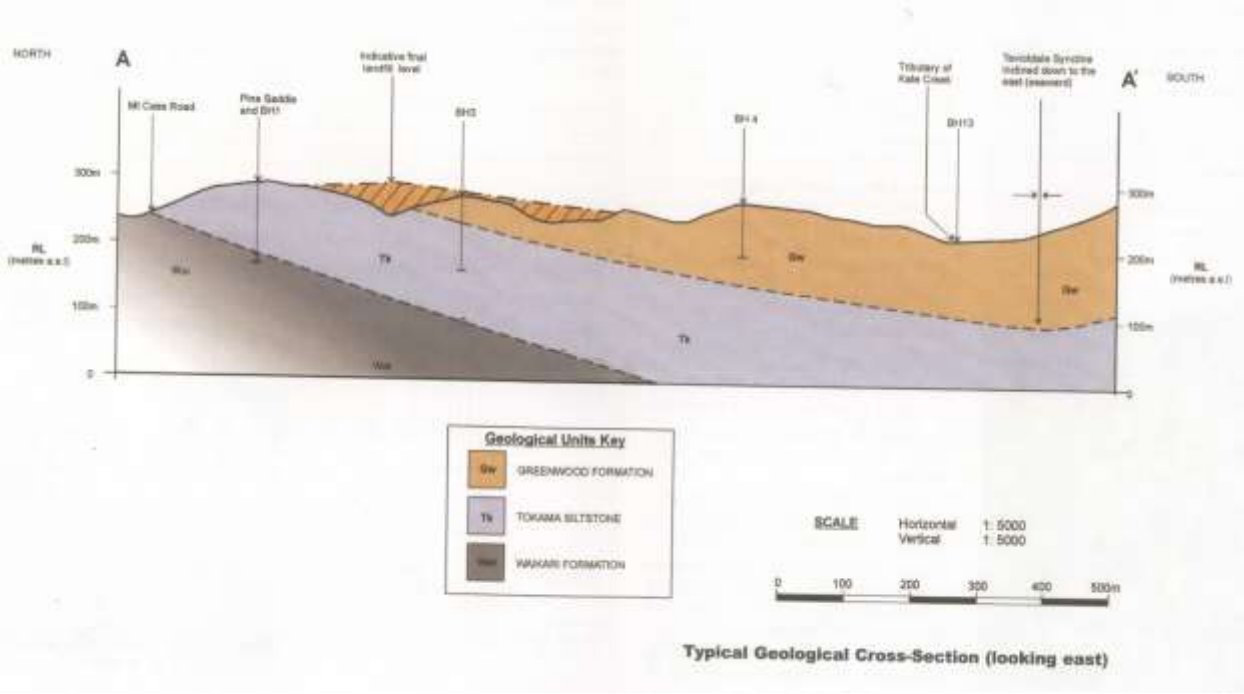

Figure 2. Cross section of geologic structure at Kate Valley (Transwaste Canterbury, 2001).

Waikari formation consists of medium to fine-sands, calcareous sandstone and hard limestone. It underlies the Tokama siltstone with no appearances on ground surface at the landfill site.

Soil samples were extracted by Transwaste Canterbury (2002) and analysed for particle size, density and porosity, Table 1. Greenwood formation sample was extracted from a depth of 3-4m below ground, and consists of predominantly fine-sands (49%-66%) with significant proportions of silt (10%-33%) and medium-sand (9%-22%) and a smaller fraction of clay (2%-9%); the results show no coarse-sand or coarse particle sizes in any of the samples tested.

Table 1. TP34 Greenwood Formation.

Description	Depth	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Silt (%)	Clay (%)
		2-0.6mm	0.6-0.22mm	0.2-0.06mm	0.06-0.002 mm	<0.002mm
Yellow-brown fine to medium sand and fine sandy-silt.	3-4m	0	9	49	33	9

The Greenwood formation was the second most porous tested soil at 34%, behind Waikari formation at 36%. More in-depth soil analysis data for the Tokama and Waikari formations can be found in the Transwaste Canterbury (2002) report.

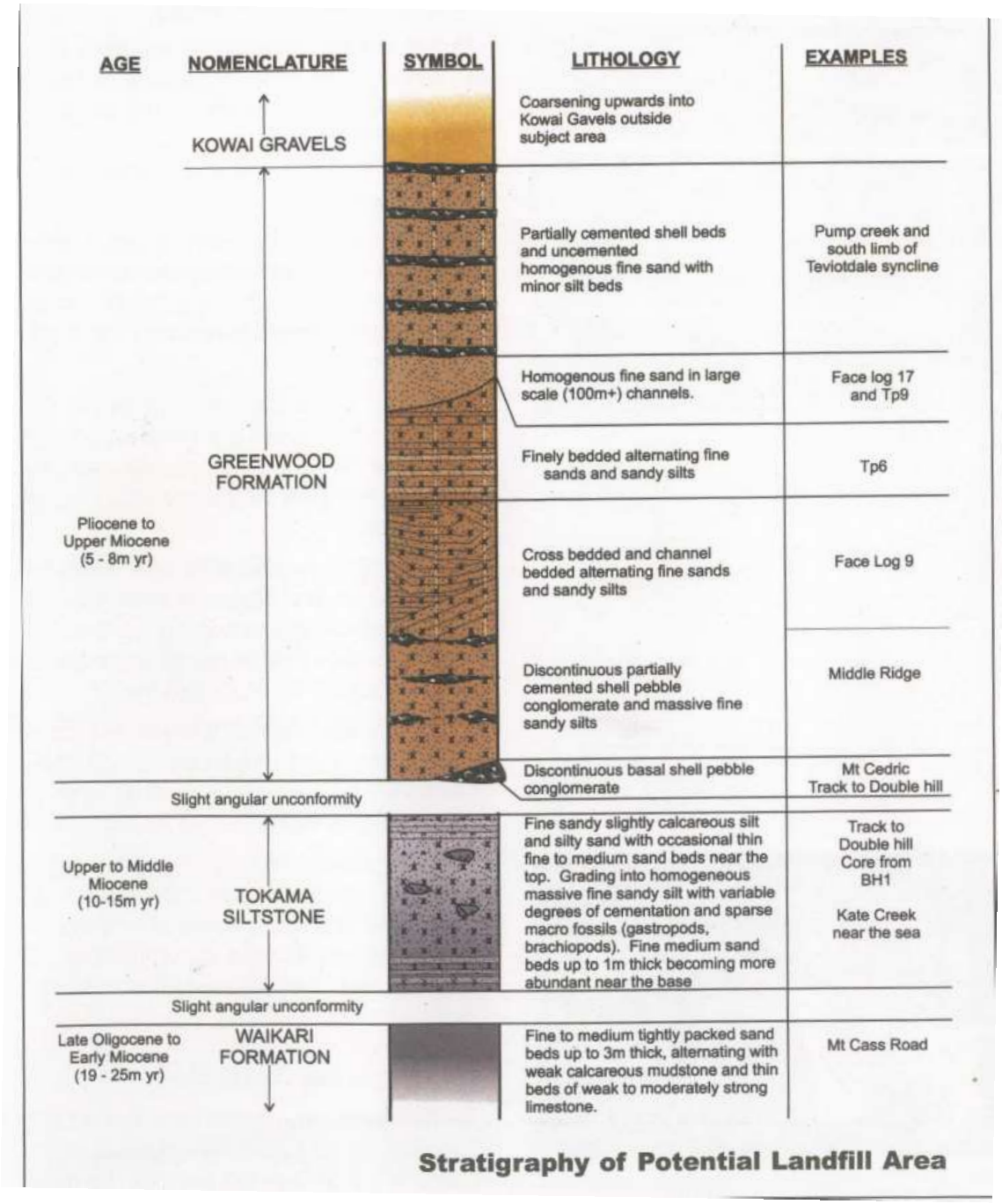

Figure 3. Geologic units of Kate Valley region (Transwaste Canterbury, 2001)

The landfill site is situated near the head of Kate Valley, between the elevations of 210m - 290m above mean sea level (MSL). Total annual rainfall varies from 213-1580 mm, with total annual averages 1000 mm (Transwaste Canterbury, 2002). Evapotranspiration in the region averages 817 mm/yr.

There are no records of water supply wells within 5 km of the landfill footprint, according to Environment Canterbury's well database. This is a reflection of the low permeability sediments forming the tertiary strata of the area. Water is supplied to the region either from surface waterways or water supply sources reticulated from elsewhere.

Figures 4-7 shows the surrounding landscape of the area in which leachate irrigation is proposed at Kate Valley, this is also where soil samples will be extracted from for experimental batch and column sampling.

Figure 4. Northern view of soil extraction area.

Figure 5. Southern view of soil extraction area.

Figure 6. Eastern view of soil extraction area.

Figure 7. South-western view of soil extraction area.

2. Literature Review

2.1. Landfill leachate characterisation

Landfill leachates are a mixture of major elements (calcium, magnesium, iron, sodium, ammonia, carbonate, sulphate and chloride), inorganic and organic contaminants (including humic acids), trace metals (Mn, Cr, Ni, Pb, Cd), ammonia-nitrogen (ammoniacal-N), xenobiotic compounds and inorganic salts, microbiological components and carcinogens (Wiszniowski, Robert, Surmacz-Gorska, Miksch, & Weber, 2006). It is important to characterise various pollutant levels within landfill leachate, this helps to identify types of treatment or removal mechanisms that are needed before discharging back into the environment. Landfill leachate at Kate valley is gravity fed into collection systems under the landfill footprint, channelling leachate into leachate detention tanks, shown in Figure 8.

Figure 8. Green leachate detention tanks (background).

Oman and Junestedt (2008) characterised landfill leachate from 12 Swedish municipal landfill sites for 400 parameters and compounds. This study identified 140 organic, metal-organic and inorganic compounds (many of which had already been previously reported), of which 55 organic and metal-organic compounds were reported for the first time. This underlines the importance of sufficiently characterising landfill leachate, as the study on leachate characterisation easily found previously untested compounds in detectable limits.

Numerous biological and physiochemical processes determine the production and composition of landfill leachates, which in most cases, is a function of waste age, microbiology, water balance of landfill, local climate and physiochemical conditions.

Biochemical oxygen demand/chemical oxygen demand (BOD/COD) is a ratio used to represent the proportion of biodegradable organics in leachate. This ratio can be used to help identify the age of landfill leachates (Fan, Shu, Yang, & Chen, 2006). A young landfill leachate usually has a higher BOD/COD ratio due to high biodegradable content, older or stable landfill leachates have a lower BOD/COD ratio.

de Velasquez, Monje-Ramirez, and Noguez (2012) characterises leachate into three categories based upon BOD_5/COD ratio:

1. Young leachates 5 years old or less with BOD_5/COD ratio $\geq$ 0.3 (biodegradable leachates).
2. Intermediate leachates between 5-10 years old where BOD_5/COD ratio is 0.1-0.3
3. Old leachates beyond 15 years in age, where BOD_5/COD ratio < 0.1.

The relationship between leachate chemical content and leachate age has been correlated in a study by Fan et al. (2006) using predictive analytics software, SPSS. The Pearson coefficient analysis shown in Figure 9 gives an indication of increases or decreases in level of chemical content and other constituents with time. Correlation values were based off of analysis results from Fan's study only, however their positive or negative correlations give an important indication of constituents' increasing or decreasing trends with leachate age. General trends show that COD, VSS, SS, TS, colour, TOC, BOD and conductivity all decrease as landfill age progresses.

Pearson correlation coefficients of chemical contents

	Landfill age	pH	COD	SS	VSS	TS	Color	TOC	BOD	Conductivity	DS
Landfill age	1.00	−0.19	−0.57*	−0.28*	−0.43*	−0.49*	−0.57*	−0.49*	−0.44*	−0.60*	−0.48*
pH		1.00	0.44*	0.02	0.10	0.42*	0.31*	0.15	0.27**	0.48*	0.42*
COD			1.00	0.34*	0.36*	0.72*	0.79*	0.64*	0.76*	0.78*	0.71*
SS				1.00	0.66*	0.29*	0.59*	0.36*	0.25	0.25**	0.24**
VSS					1.00	0.42*	0.46*	0.39*	0.07	0.39*	0.41*
TS						1.00	0.68*	0.43*	0.62*	0.86*	1.00
Color							1.00	0.55*	0.58*	0.71*	0.65*
TOC								1.00	0.54*	0.58*	0.43*
BOD									1.00	0.64*	0.61*
Conductivity										1.00	0.86*
DS											1.00

* Significance level 0.01.
** Significance level 0.05.

Figure 9. Pearson correlation coefficient (Fan et al., 2006).

Table 2 shows some contaminant levels of various landfill leachates reported around the world. This can be helpful to gain an understanding of what levels of contaminants to be

expect. The landfill values reported by Fan et al. (2006) and Chu (1994) also report the age of the landfill of which leachate was sampled from.

Table 2. Various compositions of landfill leachate from literature review.

Country	Germany	Denmark	U.S.A.	United Kingdom	Netherland	France	Taiwan A	Taiwan B	Taiwan C	JB, Hong Kong	GBD, Hong Kong
Reference	(Ehrig, 1989)	(Kjeldsen & Christensen, 2001)	(Krug & Ham, 1997)	(Robinson, 1995)	(Johansen & Carlson, 1976)	(Clement & Thomas, 1995)	(Fan et al., 2006) ***Mean value**	(Fan et al., 2006) ***Mean value**	(Fan et al., 2006) ***Mean value**	(Chu, 1994)	(Chu, 1994)
Age, yr	-	-	-	-	-	-	11-17	10	12	3.5	11
Total Ammoniacal-N, mg/L	39-3860	0.05-910	-	0.25-1560	21-292	103-1247	-	28-72	180-201	594-1610	65-883
Nitrite-N, mg/L	-	-	-	-	-	-	-	-	-	-	-
Nitrate-N, mg/L	-	-	-	-	-	-	-	9.5-20.9	2.96-26.7	0.06-0.31	21.6-179
TKN, mg/L	-	-	-	-	-	-	40.1-150	28-303	26.4-219	675-1940	137-1060
Total Organic-N, mg/L	1-670	-	-	-	-	-	-	-	-	-	-
Total Organic-C, mg/L		1-670		2.8-5690	30-1700	100-2700	-	-	-	-	-
CoD, O2 mg/L	500-60000	16-2300	50-62000	10-33700	110-9425	400-8000	*689.6	*2483.3	*3038	489-1670	147-1590
pH	4.5-9	4.5-8.6	4.5-8.2	6.4-8.0	5.9-7.0	7.8-8.4	7.03-8.50	7.30-8.40	6.82-8.37	7.2-8.0	7.2-8.4
Specific conductivity, µS/cm	-	190-8900	500-3500	503-18400	655-3380	5000-18200	3580-14160	7050-40680	5000-29600	8500-12000	2500-11800
Fe, mg/L	3-2100	0.08-180	10-1100	0.1-664	11.5-234	0.3-10	0.26-5.44	0.26-15.3	0.39-28	1.14-3.25	1.26-5.00
Cu, mg/L	0.004-1.4	0.0005-0.67	0.18-1.30	<0.02-0.16	0.008-0.085	-	0.01-4.38	0.001-1.48	0.02-0.9	<0.05	0.01-0.13
SO4, mg/L	10-1750	0.5-820	-	<5-739	10-100	<5-506	-	-	-	-	-
Mn, mg/L	0.03-65	0.01-20	-	0.06-23.2	-	-	0.18-5.27	0.02-0.74	0.02-0.75	0.05-0.24	0.05-1.30
Hg, mg/L	0.0002-0.05	0.0005-	-	-	-	-	-	-	-	-	-
TOC, mg/L	-	1-670	-	2.8-5690	30-1700	100-2700	90-439	447-1637	327-3992	-	-
Ca, mg/L	10-2500	6-660		60-1440	99-400	15-246	5.6-122	254.1-2300	70-290	-	-
As, mg/L	0.005-1.6	0.0005-0.13	-	<0.001-0.049	-	-	-	-	-	-	-
Ni, mg/L	0.02-2.05	0.001-3.2	0.10-1.20	<0.03-0.33	0.005-0.12	-	0.04-0.14	0.01-0.26	0.01-0.28	0.07-0.18	0.04-0.17
Na, mg/L	50-400	7-1000	10-3700	12-3000	34.8-462	519-2957	320-1342	297-3524	431-3142	484-1190	132-743
Cd, mg/L	0.0005-0.14	0.00002-0.030	0.001-0.130	<0.01-0.03	0.0001-0.002	-	<0.15	<0.01	<0.01	<0.01	<0.02
Pb, mg/L	0.008-1.02	0.0005-1.5	<0.1-1.40	<0.04-0.28	0.001-0.015	-	<0.02	0.0005-0.09	0.02-0.18	0.03-0.12	<0.10
Mg, mg/L	40-1150	3-430		18-470	13-96	51-271	27.8-103	23-163	15.7-157	35-63	9-26
Zn, mg/L	0.03-120	0.00005-7.2	5.3-155	<0.01-6.70	0.055-2.65	0.1-0.7	0.04-1.61	0.003-0.56	0.03-0.66	0.24-2.55	0.13-0.39
Cl, mg/L	100-5000	10-3200	10-6000	27-3410	68-680	750-2185	-	-	-	-	-
K, mg/L	10-2500	1-1100		2.7-1480	21.3-219	202-1612	198-778	184-1799	312-2243	270-632	78-416
Cr, mg/L	0.03-1.6	0.0005-1.3	0.05-1.05	<0.04-0.56	0.002-0.17	-	0.01-0.18	0.12-0.52	0.04-1.26	0.03-0.15	0.02-0.23

2.2. Landfill leachate constituent analysis

Municipal waste consists of non-recycled trash gathered from local residential or public areas. It specifically excludes industrial, agricultural, medical or radioactive wastes. The composition of waste can vary largely by area and over time; governed by the living standard or culture of residential waste producers. The type of daily waste thrown out directly contributes towards concentration and amount of leachates generated in each landfill.

It is important to consider local regional weather effects when considering landfill leachate generation as it is a major determinant on the volume of leachate collected at each landfill. Landfills in more arid and semi-arid regions will collect less leachate than areas with more annual precipitation.

Baun (2004) and Fan et al. (2006) reported the landfill leachate constituent values in Table 2 from 11 different landfills around the world of varying landfill age, operational practices and living standards. An example of this is electrical conductivity (EC) value of leachate from Taiwan A-C and Hong Kong landfills having the highest detected EC, up to 40680 µS/cm (Taiwan B); compared to U.S.A on 500-3500 µS/cm and Denmark on 190-8900 µS/cm. Discrepancies between these values can be contributed towards different landfill age, incoming waste, and seasonal effects.

2.2.1. Organic and inorganic content

Thorough tests should be conducted to gain a better understanding of the leachate (e.g. BOD, COD, Total organic content (TOC)) as Kylefors, Ecke, and Lagerkvist (2003)'s study on "Accuracy of COD tests for landfill leachates" reveal that interactions between organic and inorganic, as well as between different inorganic compounds could have an effect on COD results; it is these interaction effects that may explain why it is difficult for most landfill leachate treatment plants to achieve low effluent COD values.

Kylefors et al. (2003) also suggests that COD is no longer viable as a sole measure of organic matter, as many other substances can contribute towards COD values. Inorganic substances such as iron, sulphide, manganous, manganese, ammonia nitrogen, nitrite, and chloride may affect the value of COD; many of these exist in high concentrations in landfill leachates with sulphide and iron(II) interfering the most with COD measurements. One of their findings suggest that almost a third of detected COD concetrations could have inorganic origins.

Clay minerals have a key role in stabilisation of soil organic matter by interaction with organic matter to form complexes, making organic molecules less mobile and less likely to biodegrade (Amato & Ladd, 1992). Apart from clay content in soil, clay type can also affect the soil's capacity to bind organic matter. Clays with higher specific surface area and cation exchange capacity (CEC) adsorb more organic matter (Ransom, Kim, Kastner, & Wainwright, 1998).

Landfill leachate sorption behaviour on soil was examined by Calace, Massimiani, Petronio, and Pietroletti (2000) with respect to sorption potential based on molecular weight distributions, through experimentation by adsorption characterisation of dissolved organic matter (polyelectrolyte mixtures of components having different sizes) by means of activated carbon. It was found that behaviour of these mixtures depended partly on the molecular weight or size of particles in solution; in particular, small components are adsorbed preferentially. Structural features of the mixture change on the basis of molecular weight cut-off and may influence the mechanisms of sorption.

2.2.2. Nitrogen (NH_4-N, NO_x-N)

Nitrogen exists in leachate as ammonium nitroten (NH_4-N), NO_x-N and TKN. Cecen and Gursoy (2003) characterised leachates and showed TKN concentrations were high, with a major part consisting of ammonium nitrogen, showing that the organically bound nitrogen was already mainly hydrolysed into ammonia nitrogen. NO_x-N concentrations from Cecen and Gursoy (2003)'s study originated mostly from industrial wastes that contain nitrogen compounds.

Nitrogen may occur in the +5, +3, 0, and -3 oxidation states. It can appear in the environment as gaseous compounds (free nitrogen N_2, nitric oxide (NO_x), nitrous oxide (N_2), and ammonia $NH_{3(g)}$; or in aqueous form as nitrate (NO_3^-), nitrite (NO_2^-), ammonium/ammonia (NH_4^+(aq)/NH_3(aq)), or as organic nitrogen (van der Perk, 2006).

Ammonium levels were not tested as it is very soluble in water, but is readily adsorbed to the negatively charged cation exchange sites of colloids. Ammonium is a weak base and under basic conditions is converted into volatile ammonia following Equation 1.

$$NH_4 + \rightarrow NH_3 + H^+ \qquad (Ka = 9.24)$$

[Equation 1]

The process of ammonia into nitrate in soils is called nitrification. This process can be summarised into the 2 steps below with Equation 2 & Equation 3.

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

[Equation 2]

$$2NO_2 + O_2 \rightarrow 2NO_3$$

[Equation 3]

This process is facilitated by bacteria from the soil under oxygenated conditions; where nitrosomonas bacteria carry out the first step, the oxidation of ammonium to nitrite, and nitrobacter bacteria carry out the second step, oxidation to nitrate (van der Perk, 2006).

Nitrification reaction requires oxygen, so the reaction only takes place in well aerated soils or surface waters. As this process is facilitated by live bacteria, reaction rates are largely dependent on environmental factors such as pH and temperature. Nitrification inhibits begins below 10 °C; between 10-32°C, the reaction rates increase with temperature. Optimal pH for nitrification is between pH 6.6-8 (around the value of sampled raw leachates). The reaction is slowed at pH less than 6 and comes to a stand-still at pH less than 4.5.

Previous studies have reported ammonia to be the primary cause of toxicity of municipal landfill leachates (Clement, Janssen, & Du-Delepierre, 1997; Ernst, Henningar, Doe, Wade, & Julien, 1994). As a principal pollutant in landfill leachates, ammonia is specified by Ehrig (1989) to release from municipal solid waste over long periods of time, as opposed to soluble organics (COD).

Leachate from older landfills is rich in ammonia nitrogen due to hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates (Carley & Mavinic, 1991). Ammonia nitrogen is known to form complexes with heavy metal ions, but toxic effects in subsequent biological systems seem to be due more to the presence of free ammonia rather than from the complex heavy metals. Toxicity will differ with external factors such as oxidation, wind-drift, dilution, pH and alternations in salinity influence of ammonia concern. Chu, Cheung, and Wong (1994) determined that after a period of 3-8 years, ammonia nitrogen concentrations plateau at mean values between 500 to 1500 mg/L, remaining at this level for at least 50 years.

NO_3-N and NH_4^+-N are the main forms of N that are absorbed by plants. High inorganic N content in soil may be beneficial to plant uptake, but enhances risks of leaching from the soil profile (Shi et al., 2012). Soil physical and chemical properties strongly influence rates of denitrification, nitrification, immobilization, mineralization and leaching. Soil conditions depend on many variables including the previous vegetation, N fertilization, content of humus material, cropping systems, soil texture, temperature and precipitation (A. J. MacDonald, Poulton, Powlson, & Jenkinson, 1997).

Nitrification and mineralization rates vary as a function of moisture and clay content, which indicates a close relationship between microbial activity, clay content, soil pH and ammonium levels (Strong, Sale, & Helyar, 1999). Fine-textured soils with high moisture content are able to protect organic N from microbial attack; dry conditions will undermine the clay mechanisms leading to mineralization and subsequent nitrification of large amounts of N. NH_4^+-N can be lost from leachate, after land application, via volatilization or through adsorption in the soil.

Distribution of NO_3^--N in soil profile has been shown to strongly depend on season and the depth of sampling (Dresler, Bednarek, & Tkaczyk, 2011). Greater nitrate concentrations are normally observed in Spring than in Autumn of each year at depths of around 31 cm – 90 cm. Studies have shown that soil NO_3-N is not adsorbed by mineral-organic colloids, thus nitrate ions can easily move through the soil profile (Follet & Delgado, 2002).

The ratio of nitrification to NH_4^+ immobilization rates indicates the risk of leaching losses in NO_3^- (Cheng et al., 2013).

2.2.3. pH

pH values of medium-old landfill leachates are generally quite stable, at around pH 7-8. Low pH measurements can be an indication of young leachate, resultant from the initial production of organic acids during the acidification stage. Monitoring of pH from the same Wysieka landfill showed a nearly constant trend during the entirety of the study, with pH values varying between 7.46 and 8.61. Experiments show that soil irrigated with landfill leachate exhibited a decrease in soil pH at depths of 0 cm - 30 cm and 30 cm – 60 cm soil. Soil pH reduced in subsurface and surface soil respectively from 7.89 and 7.95 to 7.43 and 7.72, thus

pH changes were more in the subsurface soil than surface soil (Panahpour, Gholami, & Davami, 2011).

pH regulates many soil interactions including solubilisation and complexation, which affect soil organic matter stability by controlling sorption and desorption of organic carbon (van Bergen, Bull, Poulton, & Evershed, 1997).

Increasing soil pH in the range of 3.5 – 8.3 has been known to increase soil microbial activity, soil respiration and net nitrification rates in beech forests (Cheng et al., 2013; Kemmitt, Wright, Goulding, & Jones, 2006). Mineralisation and gross NH_4^+ immobilization can be affected by pH changes due to microbial population's response for both the release and immobilization of nutrients.

2.2.4. Salinity

Salinity in soil predominantly affects arid and semi-arid regions where rainfall is insufficient to leach salts from the root zone. Ash content deposited into the landfill may increase heavy metal (Na, Mg) and salt concentrations in leachate. Soils with salinity are classified into 3 categories by Brady and Weir (2002) on the basis of electronic conductivity, and SAR (sodium adsorption ratio), following US Salinity Laboratory Staff (1954).

1. Saline: ECe (measured in a saturated paste) > 4000 µS/cm
2. Sodic: SAR > 13
3. Saline-sodic: > 4dS/m and SAR > 13

EC is usually measured in a saturated paste (EC_e) or at a certain soil/water ratio (EC1:5, EC1:2, etc). However, the actual salt concentration in the soil solution, which is expressed as the osmotic potential, depends on the water content of the soil. Salinity has a pronounced negative effect on soil organic matter decomposition, irrespective of soil texture (de Velasquez et al., 2012).

Increases in soil salinity decreases the osmotic potential, reducing a plant's ability to uptake water and negatively affecting microbial activity; other stressors include high pH and ion competition limiting nutrient uptake (Keren, 2000). In sodic soils (SAR ratio > 13), Na^+ dominates cation exchange sites of soil particles. This disperses organic matter and clay particles, leading to the breakdown of soil structure and aggregates, resulting in erosion,

drying of soil and clogged pores causing hard-setting upon drying, decreasing water infiltration and permeability (Qadir & Schubert, 2002). Salinity has been shown to have a pronounced negative effect on soil organic matter decomposition, irrespective of soil texture, (Setia et al., 2011). Greater sensitivity of respiration to salinity in sandy-soils compared to finer textured soils can generally be explained by the lower water content, thus reducing the osmotic potential of the sandy-soil.

2.2.5. Metals

Study from Fan et al. (2006) analysed 13 heavy metals from leachates in Taiwan (Fe, Cr, Ni, Mb, Pb, Cd, Hg, Cu, and Zn), Table 2. This gives an indication of which common toxic metals to observe when testing landfill leachates.

Initial low pH values in young landfills from production of organic acids can contribute towards metal solubilisation. As the landfill age increases, pH increases and stabilizes, causing a noticeable fall in metal concentrations. Harmsen (1983) notes the only exception to this is Pb, as it tends to form stable complexes with humic acids. It is also necessary to keep track of humic substance in the leachate, as they have been known to enhance the transportation of heavy metals.

With respect to metal toxicity, it is most likely that the free metal ions in leachate constitute the main risk to aquatic organisms, while the colloidal and the organically complexed fractions generally are known to be less toxic (Depledge, Weeks, & Bjerregaard, 1994).

Infiltration of leachate into sub-soil strata may result in interactions that induce metal dissolution from the sub-soil matrix. Metal mobilization caused by leachate infiltration may result in groundwater contamination, even with the absence of high level metal content in the assessed leachate itself. Presence of organic matter, mainly with chelating properties with respect to cations or simply the extent of modification to pH and redox conditions of aqueous phases of the soil may extract metals through dissolution of several mineral species (Barona, Aranguiz, & Elias, 2001; Peter, 1999; Xiaoli, Shimaoka, Xianyan, Qiang, & Youcai, 2007).

2.3. Leachate quantities generated at Kate Valley landfill

Landfill leachate quantities generated at each landfill are dependent on the types of waste entering the landfill, landfill cover soil type, landfill site topography, vegetation and more so the volume of regional annual precipitation. Rainfall data for the Kate Valley region is shown below in Figure 5, where the data is obtained from NIWA's online Cliflo atmospheric database, using the data obtained from "Waipara, Wattle Grove" station (Agent Number: 4796) at latitude -43.05294, longitude 172.75972; 74m above MSL. The data is shown in monthly intervals from June 2005-February 2012, corresponding to the supplied volume data for Kate Valley's monthly collected leachate shown in Figure 11 and Figure 12.

A method for predicting landfill leachate production rates can be estimated if landfill site and local atmospheric activity data can be obtained; leachate generation is estimated by CAE (2000) with Equation 4:

$$L_0 = P - SRO - ET - DS$$

[Equation. 4]

Where: L_0 = leachate production (m^3/year)
P = precipitation (m^3/year)
SRO = surface runoff (m^3/year)
ET = evapotranspiration (m^3/year)
DS = change in leachate storage of the waste (m^3/year)

Equation 4 is used as a simple method to estimate the amount of water from rain or melting snow which will percolate through the landfill cover. It is noted that a lag between percolation time and emanation of leachate from the bottom of the landfill exists. During this lag period, landfill waste increase in moisture content until attainment of field capacity (CAE, 2000).

Rainfall at Kate Valley landfill can be seen to be very variable through June 2005 – February 2012. Highest recorded monthly rainfall through the examined period occurred on July 2008 of 192.6 mm; lowest monthly rainfall was on November 2008 at 1.6 mm, with average rainfall over the examined period being 51.78 mm per month.

Monthly collected leachate data was not available from December 2005 – February 2007, as shown by Figure 10. Average annual leachate from 2008 was 2040.3 m^3, 3267.9 m^3 for 2009, 3077.4 m^3 for 2010 and 1676.6 m^3 for 2011.

Leachate was mostly recirculated from March 2007 – May 2010, with the most leachate being recirculated back on the landfill cover soil in July 2009 of 4455 m^3. There was a brief pause on leachate recirculation between June 2010 and September 2011; recirculation recommenced in September 2011 (on a lesser scale), as shown by Figure 11.

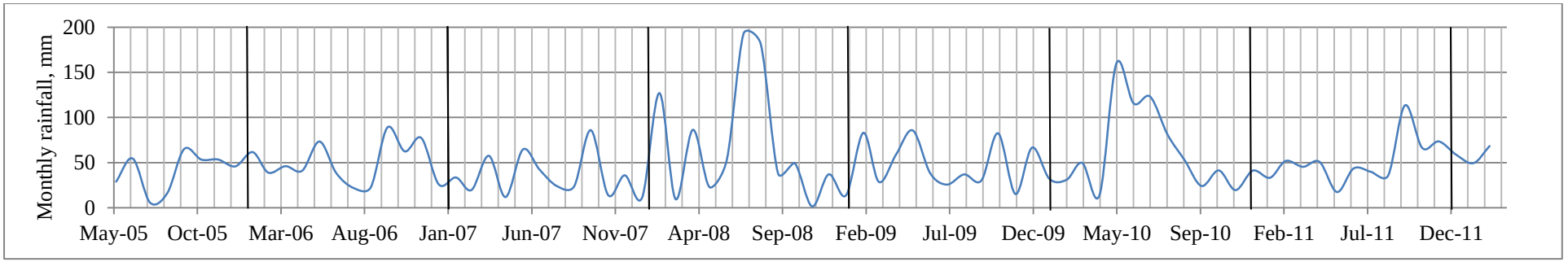

Figure 10. Monthly rainfall (mm) data collected from Waipara Wattle Grove Station (#: 4796)

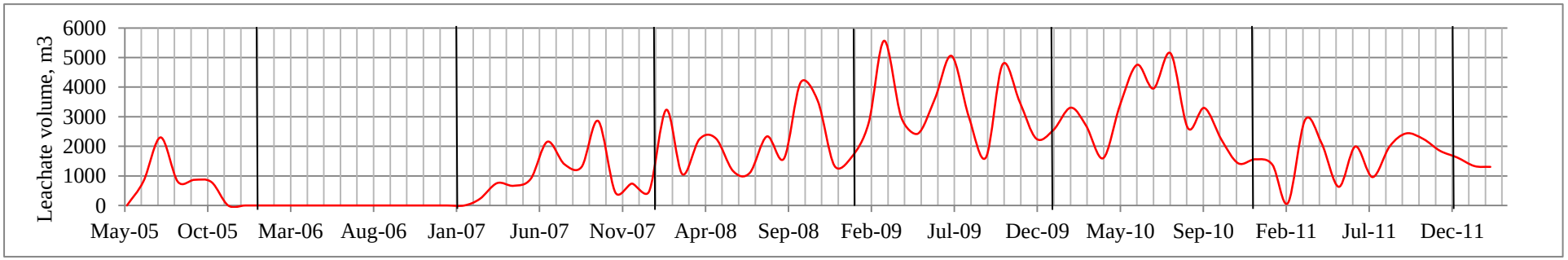

Figure 11. Monthly collected landfill leachate (m^3) at Kate Valley.

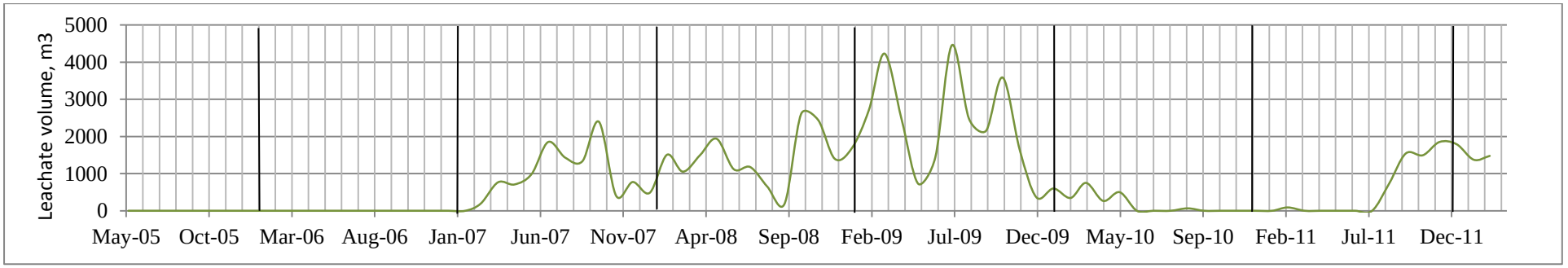

Figure 12. Monthly recirculated landfill leachate (m^3) at Kate Valley

2.4. Kate Valley leachate composition

Kate Valley leachate is generated from non-hazardous municipal waste, collected from the six residential areas of the Canterbury regional authorities. Municipal solid waste is classified by CAE (2000) guidelines as any non-hazardous, solid waste from a mixture of commercial, industrial and domestic sources. It includes garden wastes, putrescible waste, uncontaminated biosolids, clinical and related waste; municipal solid waste contains a small proportion of hazardous waste from households and small commercial premises which slip past standard waste screening procedures (CAE, 2000). Figure 13 shows a survey conducted by the Christchurch City Council in 1999 (largest of the six participating regional councils), on typical intake waste composition. The CCC waste survey was expected to reflect the waste composition of other participating regional councils.

Leachate samples were gathered from Kate Valley's leachate detention tanks, where landfill leachates are drained, then stored before disposal. Leachate grab samples were taken from these tanks during all three visits out to Kate Valley. Raw leachate samples were sent for analysis at Hills Laboratory, Hamilton, for the third sets of collected Kate Valley leachate. Table 3 below shows a comparison of sampled leachate contaminants for Kate Valley throughout this study period.

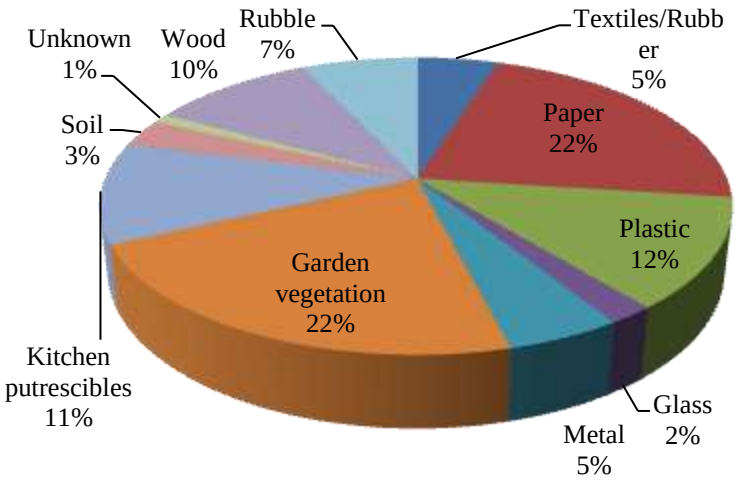

Figure 13. Waste Composition, Christchurch City Council (insert citation here).

Table 3. Kate Valley landfill leachate constituent analysis from Hill Laboratories.

Client	**Transwaste Canterbury Limited**							**Uni. of Canterbury**	
Sample collection, date	22-02-12	23-02-12	20-03-12	27-03-12	3-04-12	*6-03-12	13-03-12	14-06-13	14-08-13
Total Nitrogen, mg/L								1100	**1350
Total Ammoniacal-N, mg/L	1220	1280	1010	1070	990	*1040-1250	1350	1070	**1105
Nitrite-N, mg/L								<0.02	
Nitrate-N, mg/L								<0.02	**6
TKN, mg/L								1100	
Total Organic-N, mg/L								<60	
cBoD5, O2 mg/L				81					
CoD, O2 mg/L	2300	2100	2100	1730	1420	*1700-1870	2200		**3070
pH	7.6	8.6	9	7.7	9	*7.6-8.6	7.7		**7.89
Specific conductivity, µS/cm									**8140
Cu, mg/L	0.106	0.015							
As, mg/L	0.380	0.320							
Ni, mg/L	0.230	0.179							
Cd, mg/L	<0.0011	<0.0011							
Pb, mg/L	0.011	0.007							
Zn, mg/L	0.200	0.210							
Cr, mg/L	1.000	0.860							

*** Analysis results contain two values, taken 30 minutes apart on the same day.**

**** Analysis results completed by student.**

The collected and sampled Kate Valley leachate data from Table 3 above can be classified using NZWWA (2003)'s biosolids guidelines. This guideline can be useful for leachate application to land, as applying a waste liquid like landfill leachate will lead to similar (not identical) issues as biosolids land application.

2.5. Adsorption Theory

Langmuir's kinetic theory of adsorption states that the number of molecules striking a free unit surface area of adsorbent (soil) is directly proportional to the molar concentration of the adsorbate (leachate). Adsorbed molecules may eventually acquire sufficient thermal energy from contact with the adsorbent, and desorb. The rate of desorption depends on surface concentration of sites occupied by adsorbate (Yong, Mohamed, & Warkentin, 1992).

Partitioning or the distribution of organic chemical pollutants between leachate and soil can be described with a linear partitioning coefficient, K_d. This coefficient refers to the ratio of the concentration of pollutants remaining in pore water (Mulligan, Fukue, & Sato, 2010) as shown by Equation 5.

$$C_s = K_d C_w$$

[Equation 5]

Where:

C_s = concentration of the organic pollutants sorbed by the sediments.
C_w = concentration remaining in the aqueous phase (pore water) respectively.

K_d can be used to describe the contaminant partitioning between liquid and solid phase, only if the reactions that cause the partitioning are fast and reversible; and only if the isotherm is linear (Yong et al., 1992).

It is important to differentiate between K_d values obtained from batch and column tests. Yong et al. (1992) suggests that K_d values derived from column tests be termed as 'sorption coefficients' to reflect the performance of the soil in their natural in-situ state. Results indicate that the characteristic curves obtained from column leaching tests for example, are much lower than corresponding adsorption isotherms obtained from batch tests.

2.5.1. Batch data processing

It is often required to process reported values of contaminants from batch tests to make adsorption trends more apparent, one method of this is mg of leachate contaminant adsorbed onto mg of batched soil. In the case of this report, selected ammonia and COD values from

batch tests were calculated based on amount of contaminant adsorbed per mg of leachate onto each mg of batched soil.

Knowing the initial contaminant concentration of batch liquid, and that 30g of selected Kate Valley soil was added to 70 ml of respective batch liquid leachate, begin by calculating "x", difference between initial and equilibrium concentrations for the contaminant of concern using Equation 6.

$$x = Ci - C$$

[Equation 6]

Where:

x = difference between initial and equilibrium contamiant concentration, mg/L.

C_i = initial concentration of contaminant, prior to batch test, mg/L.

C = equilibrium concentration of contaminant after batch test, in pore volume, mg/L.

From here, mg of contamiant adsorbed per mg of soil can be calculated using Equation 7.

$$\frac{adsorbed, mg}{soil, mg} = \frac{x * 0.07\ liters}{30\ 000\ mg\ of\ soil}$$

[Equation 7]

Plotting mg of contaminant adsorbed/mg of soil (y-axis) vs. initial concentrations (x-axis), C_i will yield a linear trend if linear adsorption behaviour exists between the soil and leachate; examples of these plots can be seen in Figure 45-47.

2.5.1. Calculation of K_d, and R from batch results

From the plots produced using method from 2.5.1., the slope of the linear trend observed will be the partitioning coefficient, K_d of the soil and dilute leachate; with units of L/mg.

Knowing soil density and porosity, retardation factor (R) of contaminants in soil can be calculated using Equation 8.

$$R = 1 + \frac{\rho_d}{\theta} K_d$$

[Equation 8]

Where:

ρ_d = dry mass density (mass of dry solids divided by the total volume of the soil specimen used), kg/m^3.

θ = volumetric water content of the test specimen when the solute travels (this is the porosity when saturated) m^3/m^3.

Example: Sample calculation of retardation, R.

Assuming Kd = 0.0000009 L/kg, θ = 0.35, ρ = 1780 kg/m^3

$$R = \left[\frac{1780\frac{kg}{m^3} * 0.0000009\frac{L}{mg} * \frac{m^3}{1000\,L} * \frac{1\,000\,000\,mg}{kg}}{0.35}\right] + 1$$

R = 5.58

2.5.2. Calculation of K_d, R, and pore volume from column results

In the case of column tests, pore volumes can be calculated knowing the volume of soil in the soil monolith and soil porosity. The first step is to plot a graph of pore volume concentration against pore volume (PV, unitless), such as that in Figure 64. Breakthrough is noted on Figure 64 as the inflection point, where loading on soil begins to reach capacity. The number of pore volumes (unitless) at this point is equal to the retardation factor, and using Equation 8, one can calculate the K_d value for the column, based on the loading characteristics of this contaminant.

In order to determine this, start by finding the soil volume of the soil monolith.

Volume of soil in the soil monolith can be calculated from Equation 9.

$$\text{Soil volume} = \pi r^2 * \text{H} * 1000$$

[Equation 9]

Where:

Soil volume = volume of soil in the soil monolith, Litres.

r = circular radius of soil in soil monolith, meters.

H = height of soil in soil monolith, meters.

Pore volumes (Litres) can be calculated from Equation 10.

$$Pore\ Volumes, Liters = porosity * Soil\ volume$$

[Equation 10]

Where:

Porosity = porosity of in-situ soil, $m^{3/}m^3$.

Pore volume (unitless) can be calculated using Equation 11.

$$Pore\ Volumes, Unitless = \frac{cumulative\ drainage, Liters}{Pore\ volumes, Liters}$$

[Equation 11]

Where:

Cumulative drainage, Litres = collected cumulative pore volume from column.

Knowing the number of pore volumes (unitless) for contaminant breakthrough in respective soil columns is equal to retardation factor, R; the partitioning coefficient can be calculated using Equation 8.

2.6. Land discharge benchmarks in New Zealand

Many arid regions around the world have already been practicing application of landfill leachate to land or forested crops; this has been mainly to help alleviate the use of valuable water resources. The rules and practices that govern the application quantities or treatment required for the leachate before land application can vary from region to region. These variances are a result of different climate, input waste, landfill operational practices and landfill age, all contributing towards the composition of landfill leachate. Various organisations around the world have studied and analysed benchmark values for various

pollutants for application of wastewater to land. The most notable and used of these is from the USEPA.

In New Zealand, Clinton, Wang, and Magesan (2010) of Scion, a biomaterials research organisation, have published a best management practice guideline: "Best management practices for applying biosolids to forest plantations in New Zealand". The need for this document was apparent as there previously was no document (in New Zealand) for the specific regulations which govern all aspects of biosolid preparation and use, to assist with the critical legislation in New Zealand (Resource Management Act 1991). This document builds on research from USEPA, but put within a New Zealand context. Covered material includes site management, selection, contingency plans and guideline ceiling values for various pollutant concentrations in soil.

Useful information from Clinton et al. (2010) includes the recommended maximum soil acidity of pH 5.5. This was set to minimize risks associated with phyto-toxicity within the soil, or excessive metal uptake by crops.

Guideline values for nitrogen loading are generally set based upon agronomic nitrogen needs of crops, which is known to be conservative due to the fact it does not account for mechanisms of nitrogen loss in soil such as mineralisation or denitrification. Clinton et al. (2010) has set the NZ nitrogen loading guidelines as 200 kg of total N/ha/yr, with the recommendation that large or long-term application rates of nitrogen should be largely based upon site-specific assessments of soil characteristics, mineralisation rates, climate, and agronomic N needs of crops (if any).

Table 4.2 (Appendix A: 1.) from Clinton et al. (2010) also contains recommended ceiling limits for heavy metals in soil, and ceiling limits for biosolids, split into two grades of stabilisation, A and B. Grade A is a more treated or 'cleaner' biosolid, with extensive pathogen and vector attracting compounds removed, Grade B are those that are less treated than Grade A.

Although the biosolids guideline did not mention limits for soil and leachate salinity or conductivity, a study of sustainable landfill leachate irrigation practices at the Newington Landfill (Australia), conducted by Bowman, Clune, and Sutton (2002) suggests a conductivity roof value of 3600 µS/cm for applied leachate. This value was based on field testing and with consideration from the ANZECC guidelines, a set of guidelines developed

by the Australian and New Zealand Environment and Conservation Council (ANZECC). The purpose of this guideline is to provide an authoritative guide for water quality targets, required to preserve and sustain current or likely future, environmental values for use of natural and semi-natural water resources in Australia and New Zealand. The document sets methods for limits on pollutant concentrations in freshwater, coastal and marine environments.

Since soil ceiling values are given in terms of recommended maximum allowable concentration, it will be required to compare these to Kate Valley leachate. Experimental tests would need to follow to determine loading capacities of Kate Valley soil to various leachate dilution strengths.

2.7. Landfill leachate land application rates and practices

Irrigation management practices can have a significant effect on the success of implemented irrigation schemes. These management practices can range from spray equipment aspects such as drip or spray irrigation, to other management aspects such as irrigation frequency, irrigation volume, rotational irrigation schemes and allowed recovery time between irrigation applications. It is difficult to directly compare the metrics used in these management practices due to the largely varying factors affecting their outcome between each study case; e.g., different soil chemical and physical properties, land-use history, varied constituents of applied leachate and regional climate. It is best to examine existing management practices through a case-by-case basis, where only potentially useful management and loading practices will be reviewed.

2.7.1. Ottawa County Landfill, Michigan.

In a study conducted by N. W. Macdonald, Rediske, Scull, and Wierzbicki (2008), landfill leachate from the Ottawa County landfill site was irrigated on landfill cover soil. Applications of leachate occurred once a week at a rate of 2.14 cm per application between July - November 2003. Following that, soil plots were irrigated once every three weeks between June - September 2004-2006 at mean rates ranging from 1.01 to 1.44 cm per application. These practices were determined from N. W. Macdonald et al. (2008)’s May 2003 study, conducted on landfill cover soil quantifying the operational effects of landfill

leachate irrigation. Soil response was determined through sampling and analysis of the top 50 cm of cover soil, collected in October of each irrigation year.

Constituent deposition rates on the irrigation plots were examined by N. W. Macdonald et al. (2008). Recommendations include the need to apply leachate at periods of highest evapotranspiration demand; this is primarily to reduce the potential for high solute leaching losses. High NH_4^+-N deposition in 2003 (961 kg N/ha) increased the risk of NO_3^--N losses to groundwater and the potential for its movement off site. As a result of implementation of spray area rotation, constituent deposition rates were greatly reduced in 2004 – 2006, as shown in Appendix A. N. W. Macdonald et al. (2008) reported no adverse effects on the environment from nitrogen loading, which was expected as it was much lower than Bowman et al. (2002)'s reported value of 1300 kg of N/ha/yr, also with no adverse effects on soil.

Further recommendations by N. W. Macdonald et al. (2008) include keeping spray leachate application below 2.4 cm per irrigation event. Mean application rates for Ottawa County's rotational schedule between 2004-2006 ranged from 5 - 8.6 cm, exceeding Jones, Williamson, and Owen (2006) recommended sustainable undiluted leachate application rate of 2.5 -5.0 cm/yr. The exceedance in loading rate was justified by Ottawa County's rotational irrigation schedules, reducing total irrigated volume per section through a three week resting period between successive leachate irrigations. Continuous monitoring of leachates and receptive soil and environment is highly recommended to detect any adverse effects from long term application and to implement adaptive or remediative measures.

2.7.2. Riverbend Landfill, Western Oregon

In Western Oregon, the Riverbend landfill has had success with saline (total dissolved solids (TDS) 777-6940 mg/L, Chloride 180-1760 mg/L) landfill leachate irrigation onto poplar plantations since 1993. Smesrud, Duvendack, Obereiner, Jordahl, and Madison (2012) investigation is relevant to this research as it discusses various best management practices to avoid detrimental long term effects from leachate application to land; for example, overloading may not be evident in vegetation response until several irrigation seasons have past.

Primary salinity issues that have to be addressed with poplar tree irrigation are soil response to application of TDS, boron and chlorides. Given the leachate constituent strength and

irrigation plot selected, salinity was determined to be the limiting constituent in the Riverbend irrigation scheme.

With over 15 years of record monitoring and operational data. Smesrud et al. (2012) has largely credited its success at irrigating a range of different leachate concentrations through the years to its adaptive management techniques.

Drip and spray irrigation are the two main methods of liquid dispersion onto soil. Riverbend installed both types of irrigation equipment to explore their respective performance and suitability for their irrigation practice. Riverbend's spray irrigation equipment consisted of a pump, coarse screen filter delivering water to a rotating micro-spray sprinkler head. This delivered irrigation leachate in a uniform manner through the area, up to an application rate of 4.6 mm/h. Drip irrigation consisted of a pump, coarse and fine filtration on a closed loop distribution system, with the option of chemical injection to meet pH and Cl_2 benchmark targets. Their drip system irrigates at 0.69 mm/h, over six times slower than that of the spray irrigation.

Smesrud et al. (2012) noted that drip irrigation required more attention for long-term soil salinity issues than spray irrigation. This was accredited to the need for periodically changing drip irrigation locations to avoid accumulations of salinity in soil profile. Drip irrigation was noted as having a much lower irrigation rate, and the distribution of applied water is more concentrated within the immediate soil below each drip emitter and along a linear zone of wetted soil along each drip tube.

Although spray irrigation is effective at quickly applying a large volume of irrigation leachate over a uniform area, drawbacks of the equipment include overspray of leachate, coming into contact with vegetation leaves, causing stress with saline waters when in contact with young trees. Drip irrigation systems are useful in this respect, as overspray is eliminated and application is only applied to desired tree root areas.

Selection of resilient poplars, tree stand spacing, poplar thinning and harvest rotations are critical to maintaining a productive tree stand that is resilient and resistant to polluted leachate irrigation. The most applicable of crop management techniques to the Kate Valley study was the altered nitrogen loading rates for differently aged poplars. Poplar cuttings (clones) less than a year old had 0 kg N/ha/yr applied, 111 kg N/ha/yr for trees aging within

1-2 years, 196 kg N/ha/yr for 2-3 years, 339 kg N/ha/yr for the 4-5 years and 357 kg N/ha/yr for poplars five years and above.

2.7.3. SCION BMPs and NZ Biosolids Guidelines (SCION)

Classification of biosolids using NZ Biosolids guidelines is done based on biosolid stability and contaminant grades into 2 main categories: "Unrestricted use" (Aa) and 3 types of "restricted use of biosolids", (Ab, Ba, Bb). The leachate from Kate valley is classified under "Restricted use "B" as it does not employ any of the pathogen reduction processes, vector attraction reduction methods, or product pathogen standards listed for classification A. Based off of metal concentrations shown in Table 3 above, soil limit classification for Kate Valley leachate is 'b', as all metal concentrations are below the set maximum concentration weights. No organic testing information was conducted for the constituents listed for classification, but it is assumed none of these exceed the limit values. The Kate valley leachate is classified with the NZWWA (2003) as a "Restricted Use, Ab" biosolid.

The SCION (2010) "Best management practices for applying biosolids to forest plantations in New Zealand" is a comprehensive guideline covering BMPs on site evaluation, consent process, implementation, monitoring and reporting of biosolids application to forest plantations in New Zealand. The document largely compliments the "ceiling-values" given for biosolids in NZWWA (2003)'s "Guidelines for the safe application of biosolids to land in New Zealand".

Implementation of SCION (2010)'s guidelines cover the various methods of biosolids dispersal and application rate and timing, along with a short review of their strengths and weaknesses. SCION notes that nutritional benefits of biosolids applications for forest planations can only be achieved through proper adaptive management of their application. Applications to forest sites can be made annually or once every several years. Irrigating every several years can minimize operational costs of irrigation, as well as provide time for the plants and the environment to assimilate the biosolids. An example of this is Rabbit Island in Nelson, where liquid biosolids from the nearby wastewater treatment plant are applied to pine plantations every three years. Other factors which determine loading rate and frequency include local climate, precipitation and existing levels of nutrients and pollutants in the soil and water.

Successful and sustainable biosolids application to forests requires application rates which do not exceed the nutrient uptake requirements of trees. Over-applying biosolids can result in leaching of nutrients into local nearby water resources. The most important nutrient, and often the limiting factor of biosolids application, is nitrogen. NZWWA recommends up to 200kg/ha/yr of nitrogen, but the Riverbend and Ottawa case studies have shown that this limit can be exceeded dependent on receiving tree species, their age and other management practices such as dilution and land rotation irrigation.

Phosphorus nutrient is generally as large of a concern as nitrogen, however the concentration needed by plants is only about 20-50% that of nitrogen and levels are low in landfill leachate, thus application rates set on nitrogen needs will seldom limit plant growth. Issues with nitrogen leaching usually occurs from high nitrogen loadings under the assumption that there is sufficient P levels in soils; phosphorus accumulation in soil may occur, but the amount is negligible when considering the soil's capacity to bind phosphorus, P levels in soil is also usually highly variable given site topography, past land activity and drainage, etc. Due to this lack of P to compliment N in the soil, plant uptake of N is less likely to occur due to insufficient P, leading to leaching and runoff of N.

Monitoring and reporting practices outlined by SCION include pre and post monitoring of biosolids application. Pre-monitoring includes non-biased sampling of surrounding soil and water, to examine existing nutrient and pollutant loadings. Although it is noted that this is not explicitly required for the application of resource consent, it is strongly advised as it gives an indication to existing condition of the environment, and their respective resiliency and capacity to bind constituents. Post-biosolids application monitoring of soil and water resources exists with a similar nature, where periodic-continuous monitoring of soil is recommended to identify any long-term adverse effects biosolids applications may have on soil. Sampling of soil in biosolids applied areas can be tested along with non-application areas to gauge the immediate effect of contaminant loading on the soil. Sampling of heavy metals in soil should analyse the surface 20 cm of soil for metals such as As, Cd, Cr, Cu, Pb, Hg, Ni and Zn. pH sampling of soil can also be an indication of heavy metal leaching in soil as it is related to their availability. Post-application monitoring of any water resources can be conducted on water samples collected from downstream of applied areas and comparing that with those collected upstream, which act as a control sample.

3. Methods

3.1. Site Visits

Table 4 summarises all the site visits to Kate Valley for the duration of the thesis work, inclusive of samples collected.

Table 4. Summary of Kate Valley landfill site visits.

Date of visit	Samples collected
17 April 2012	Landfill leachate and disturbed soil samples.
5 October 2012	Disturbed soil samples to a depth of 1 m (with soil auger); landfill leachate.
14 June 2013	Extracted 4 in-situ soil monoliths; landfill leachate

3.2. Sample collection and experimental setup

3.2.1. Ex-situ soil sample collection

Ex-situ (disturbed) soil samples were taken directly from site at Kate Valley (5 October 2012) with a soil auger as shown by Figure 14. These were either extracted using a soil auger, or directly with a shovel. The patch of land which all soil samples were taken from consisted of flat land with no slope. The patch of soil was vegetated with grass and weeds, with no significant tree growth immediately beside it; it fully exposed to sunlight. The patch of land was not part of any runoff channel or flow path, but soil samples remained relatively moist on the day of sample collection, given prior precipitation the day before. Samples were collected at various incremental depths, and were collected for use in experiments such as volatile solids tests, sieve analysis, and to be sent away for preliminary soil analysis with Hills laboratory.

Figure 14. Ex-situ soil extraction with soil auger.

Weather during the initial site visit and preliminary sample collection was sunny, with no immediate previous precipitation activity. Soil was relatively dry within the first 30 cm of depth.

Weather during collection for in-situ soil monoliths (14th June 2013) was also overcast, with moist soil conditions from precipitation activity 3 days prior.

3.2.2. Column extraction

Column extraction closely follows the method disclosed in Cameron et al. (1992)'s research on in-situ soil monolith extraction. A few amendments have been made to column construction in the laboratory, after extraction from the field; namely the installation of the bottom gravel layer within the soil monolith.

Before extraction of soil monoliths in the field, some equipment and preliminary preparation is required to make the equipment needed for extraction.

Portable mobile heating equipment is needed in the field for heating the Vaseline to 60°C liquid form for pouring into the gap between soil and column casing. This was conducted

with the use of a car inverter and an IEC (brand) 220/240V AC portable electric element heater. A vehicle was driven close to the excavation site for heating.

For the column case construction, Iplex Pipeline's "Farmtuff culvert" pipe was used. The pipe was 6 mm thick with an inner hollow diameter of 230 mm. They were purchased in 1500 mm lengths, and subsequently cut into 450 mm for each column. A circular inner plastic of thickness 5 mm was silicon glued to inside bottom surface of the column case; this was to allow the space for pouring in the Vaseline sealant, once soil has been excavated. This circular inner plastic thickness was tapered at 45° to help with soil penetration during excavation, Figure 15.

Figure 15. Empty soil monolith casing.

The bottom plastic plate was purchased as 5 mm thick sheets, and cut into 250 by 250 mm squares. A threaded hole was drilled in the centre of the plate, 12 mm diameter wide. This is where the irrigation fitting was installed for gravity drainage.

The soil monolith extraction method is as follows:

1. Place the Vaseline on the heating element at 60°C, in preparation for column sealing.
2. Find a relatively flat soil surface to extract multiple soil columns, with plenty of space all-around the selected patch.
3. Place column casing on the soil surface, and press firmly onto the soil, sharp edge of the column facing down.
4. With a shovel, carefully dig to a depth of 100 mm around the circular column.
5. Push the column casing down into the soil as shown by Figure 16. Take care to minimize any horizontal movement of the column, as this may disturb the circular soil core, encased within the soil column.

Figure 16. In-situ soil columns ready before insertion of bottom plate.

6. Repeat steps 3-4 until the soil is around 10cm from the top of the soil column casing.
7. Place a funnel in the gap between the soil core and the column casing. By now, the Vaseline sealant should have been heated into liquid form,
8. Gently pour in the liquid Vaseline until it barely reaches the soil surface, Figure 17.
9. Let the column and Vaseline set for 5 minutes, Figure 18.
10. Place the metal extractor plate, flat on the bottom of the column.
11. Using an iron crowbar, wedge the metal extractor plate, just below the bottom of the column.
12. Once the metal plate has been wedged past the cross-section of the soil monolith, lift the soil monolith from the ground, and place it into the transport vehicle.
13. Shift the soil monolith from the metal bottom plate to a plastic casing plate.
14. Taking extra care, secure the soil monolith and plate to the vehicle, ready for transport back to the laboratory.

Figure 17. Pouring heated liquid Vaseline into the space between soil and column casing.

Figure 18. Dried solid Vaseline.

During transportation from Kate Valley to the laboratory, it is important to minimize road-shock, as this can disturb the in-situ soil column, and may even create cracks within the soil monolith. A general reduction in speed and avoidance of on-road holes was sufficient to safely transport the columns back.

As shown by Figure 20, the fitting for a drainage pipe was threaded through the previously drilled hole on the bottom plate, once the bottom plate had been attached to the column monolith, and set upon the stand. The 6.5 mm polyurethane delivery tube was cut into the desired lengths, and subsequently inserted into the drainage fitting when the columns were ready for irrigation.

3.2.3. Column setup

After transportation of soil monoliths back to the laboratory, a drainage layer of gravels was deposited on the bottom of the column, before sealing the bottom plate, ready for column saturation. The steps in this procedure were:

1. Place a soil support mould on the top of the soil monolith.
2. Invert the soil monolith (carefully).
3. Remove the plastic plate, exposing the bottom surface of the soil column.
4. Hollow out ~ 40 mm of soil with a smade.
5. Washed gravel was placed in the recently hollowed space.
6. Cover the gravel surface of the column with the previously detached plastic cover plate, and invert the column once again.
7. Seal the contact point between the soil monolith case and the plastic plate with silicon sealant.
8. Leave for 24 hours to dry, before use in experiments.

After the drainage layer was made within the soil monolith, they were placed in a 21°C temperature controlled room, ready for experimentation. The steps here were:

1. Set the columns on a custom-made steel frame stand, as shown by Figure 19.
2. Attach the drainage fitting to the exposed bottom of the column monolith casing, as shown by Figure 20.
3. Direct the drainage tube into the drainage bucket.
4. The valve is switched to ‘on’, and the soil monolith is ready for saturation and leachate application as shown by Figure 21.

Figure 20. Soil monolith laboratory setup.

Figure 19. Drainage valve fitting on bottom of soil monolith.

Figure 21. Single soil monolith laboratory setup.

3.2.4. Soil monolith saturation

Extracted soil monolith columns were saturated with de-ionised water before irrigation with leachate, as shown in Figure 22; This was to ensure no impermeable layers exist within the soil monolith.

1. Noting the time, apply 2 litres of de-ionised water onto each participating column.
2. Wait 24 hours to ensure water has ceased to flow out of the column.
3. Weigh the final water drainage volume.

Figure 22. Bird's eye view of soil column mid-irrigation.

Comparisons between the irrigated 2 litres of water and the final water pore volume can give an indication of saturation within each column. Pore volumes between multiple columns should roughly be equal; columns with noticeably higher final pore water volumes may

indicate severe flow preferentiality, an unsealed edge, or short circuiting through the soil monolith.

A transparent semi-flexible plastic "barrier" can be seen in Figure 22, this was placed within the inner diameter of the column to intercept any irrigate from spraying outside the column's diameter. This plastic barrier was very light, thus did not damage soil surfaces or the Vaseline sealant perimeter.

3.3. Experiment methodology

3.3.1. Batch test experiment method

Preliminary batch test experiments were conducted before column tests to evaluate soil sorption potential. This was conducted for various cases of leachate strength and layers of soil, detailed in Table 5.

Table 5. Summary of batch solution and soil types tested.

Batch solution tested	Soil type tested
Raw leachate	0 – 200 mm soil depth
5x leachate dilution	200 – 400 mm soil depth
10x leachate dilution	400 – 600 mm soil depth
20x leachate dilution	
50x leachate dilution	
De-ionised water	

Assuming respective leachate solutions and soils are ready for use, the batch test experiment method followed the following steps:

1) Measure out 30g of the desired soil and place in 100 ml batch test containers.
2) Fill each container to 100 ml with appropriate leachate solutions.
3) Tightly fasten the cap and label each batch container.

4) Place the batch containers on the rotational agitator, Figure 23. Secure them with tape if necessary, as containers may dislodge during agitation.
5) Set the rotational apparatus to spin at 60 rpm, with batch bottles placed 25 cm from the centre of rotation. When all batch containers are secure, turn on the apparatus and leave for a 24 hour agitation period.
6) Turn off the machine after 24 hours of agitation and remove all batch containers from the apparatus.
7) Let the batch containers settle for an hour, before transferring them into centrifuge containers for separation. This step is to separate the soil from the leachate solution.
8) Once the centrifuge containers are prepared, place them in the centrifuge, set at 4000 rpm, and run the centrifuge for 10 minutes.
9) After centrifuge, remove the centrifuge containers and proceed to filter each sample through disposable 0.45 micron filter, using a disposable syringe.

Figure 23. Rotational agitator.

After filtration, samples are refrigerated at 4°C until analysis. All samples were analysed within 1 week of refrigeration.

3.3.2. Column experiment

Column experiment method details the procedure involved with leachate irrigation and pore volume collection for sampling purposes.

Given the scope of this experiment and past research (Bowman et al., 2002; N. W. Macdonald et al., 2008; SCION, 2010); it was decided that 40 mm of sample will be flood irrigated with each irrigation event. This involves measuring out the correct volume of

application and gently pouring it over the top surface of the column; this avoided dislodging any surface soil particles.

With the column equipment dimensions, the irrigation volume equates to 1520 ml of leachate application.

The column irrigation method is as follows:

1. 40mm of irrigation will be prepared in the reservoir for each respective soil column.
2. Noting the current time, turn on the peristaltic pump, irrigating each column. This will continue until all 1520 ml of sample in each reservoir is drained. The sample will be allowed to drain through the column.

From the noted time in Step 2 of the column irrigation method, samples will be collected at 2 subsequent time intervals. This usually occurs at 3-4 and 7-8 hours after each irrigation event; these times are derived from trial columns conducted from Kate Valley soils, these times will vary when using different soils of different physical attributes.

For pore volume sample collection, the method is as follows:

1. Noting the current time, place a sample collection cup at the outlet of the delivery tube from the bottom of the column monolith. Allow collection of at least 40 ml of sample.
2. While the pore volume samples are being collected, weigh the amount of pore volume in the collection buckets for each column, Figure 24.
3. Once 40 ml of pore volume sample is collected for the column, note down the final time.
4. Sample pore volumes are subsequently weighed, converted to volumetric units (m^3) and added to the total pore volumes collected at the end of sample collection. Collected samples were immediately refrigerated at 4°C until analysis. Samples were stored no longer than 2 weeks before analysis.

Figure 24. Soil monolith pore volume collection set-up.

Termination of leachate application for each column varied based on time constraints and analysed results. This will be discussed further in section 6.0 Column experiments.

3.3.3. Bromide column experiment

The Bromide column experiment followed the same convention as the column experiment with respect to irrigation volume (40 mm, i.e. 1520 ml), irrigation method (spray), collection systems and sample storage (refrigeration at 4°C).

Bromide was introduced to the column through the dilution of high concentration (20000 mg/L) potassium bromide (KBr). KBr was diluted to 200 mg/L each time with de-ionised water. KBr irrigation was scheduled once every 2 days.

3.3.4. Column dissection

Column dissection involves opening up the soil monolith structure after testing had concluded. This was done to examine soil saturation and extract soil samples at various depths for analysis at Hills Laboratory. Before starting column dissection, all liquids must have already been gravity-drained from the column monolith.

The Method used for soil dissection was as follows:

1. Disconnect the irrigation fitting on the bottom of the soil monolith from the experimental set up.

2. Place the soil monolith on a cleared table, with room and easy access to the sides of the soil monolith.
3. Using a craft knife cut away the silicon used to seal the soil monolith.
4. Using an angle grinder, make 2 cuts through the thickness of the pipe, on opposite sides of the round column and pull open the casing, Figure 25.
5. Manually pull away one side of the column casing, and brush away the soil to expose the middle face of the soil column, Figure 26.

Figure 25. Soil monolith with half of casing pulled off.

6. Take photographic evidence of all aspects of the soil column and conduct critical examination of all parts of the soil column, then extract soil samples from the soil monolith.
7. Dispose of remainder unused soil safely.

Figure 26. Cross section of a soil column.

3.4. Soil analysis methods

3.4.1. Soil sieve analysis

Soil sieve tests were conducted from collected disturbed Kate Valley soil samples. This was to gain an understanding of soil physical properties such as particle size distribution, which gives an insight into the amount of soil particle surfaces, hence the available soil surface for adsorption.

Disturbed soil samples were collected from Kate Valley on 5th October 2012 using a soil auger, as shown by Figure 17. 4 soil samples from different depths into the ground were collected: 0-5 cm, 5-20 cm, 20-40 cm, and 40-60 cm depth.

Endecotts Ltd soil sieve trays were used in 4 sizes, these were: >0.840 mm, > 0.600 mm, >0.187 mm, <0.187 mm.

The method of sieving for each depth increment of soil sample was as follows:

1. A weighing plate was placed upon the weight sensor, and then zeroed.
2. 500g of dried soil sample was put on the plate using a spoon.
3. The measured soil was then poured into the top-most layer of the clean, dry sieving apparatus.
4. The sieving apparatus was manually agitated in all lateral directions with moderate force, for 10 minutes.
5. The amount of soil retained in each layer of sieve was measured using the weight sensor, and recorded. Large particles of soil retained in the top-most layer that did not break down from manual agitation, were not manually forced through the sieve.
6. A final check is conducted to see if the individual weights of each soil layer summed to the original 500 g weight measured at the start.
7. Soil lost (%) can be calculated from Equation 12. A maximum of 5% soil loss is acceptable; if soil loss exceeds 5%, the soil analysis is repeated again more carefully until a value below 5% is obtained.

$$Soil\ Loss, \% = \ 1 - \frac{initial\ soil\ weight, g}{final\ soil\ weight, g} * 100$$

[Equation 12]

Results were compared with those found using Transwaste Canterbury (2002)'s classification, as follows:

- Coarse sand (%), 2 mm – 0.6 mm
- Medium sand (%), 0.6 mm - 0.22 mm
- Fine sand (%), 0.2 mm – 0.06 mm
- Silt (%), 0.06 mm – 0.002 mm
- Clay (%), <0.002 mm

  Note that the soil sieving done for this study was not able to distinguish between fine sand, silt and clay.

3.4.2. Soil fixed and volatile solids

The fixed and volatile solids tests follows the procedure outlined by APHA, AWWA, and WEF (1989).The remaining solids after incineration, represents the total fixed, dissolved, or suspended solids; while the weight lost on ignition is the volatile solids.

Equation 13 and 14 below are used to calculate mg/L of volatile solids and fixed solids respectively.

$$mg\ volatile\ solids/L = \frac{(A-B)*1000}{sample\ volume,mL}$$

[Equation 13]

$$mg\ fixed\ solids/L = \frac{(B-C)*1000}{sample\ volume,mL}$$

[Equation 14]

Where:

A = weight of residue and dish before ignition, mg.

B = weight of residue and dish or filter after ignition, mg.

C = weight of dish or filter, mg.

3.4.3. Soil porosity

Soil porosity experiment is conducted on in-situ soils to gain an understanding on available pore space within the tested soils.

The porosity mould is a hollowed, cylindrical metal case. The inner diameter of the cylindrical case is 60 mm diameter wide by 58 mm tall; as shown by Figure 27.

Figure 27. Soil porosity metal column mould.

The experimental method follows:

1) Measure the weight of the cylindrical column mould.
2) Press the column mould into a sample of collected soil monolith in-situ soil (A spare collected in-situ soil column monolith was used, small casings of soil was pressed from the middle of the soil monoliths, thus it was assumed these porosity soil samples retained in-situ structure).
3) Protruding soil above and below the metal casing is sliced off to produce a flat surface, sitting flush with the surface ends of the column casing, Figure 28.

Figure 28. Porosity mini-column extraction from failed soil monolith.

4) The combined initial weight of soil and column mould is weighed.
5) The soil and column mould is placed in an incubator at 40 °C for 48 hours to fully dry.
6) The combined dry weight of soil and column mould is weighed.
7) Clear parafilm was used to cover one end of the soil-mould, and secured on with rubber band.
8) The soil is then submerged under de-ionised water, entirely, for 24 hours to fully saturate, Figure 29.

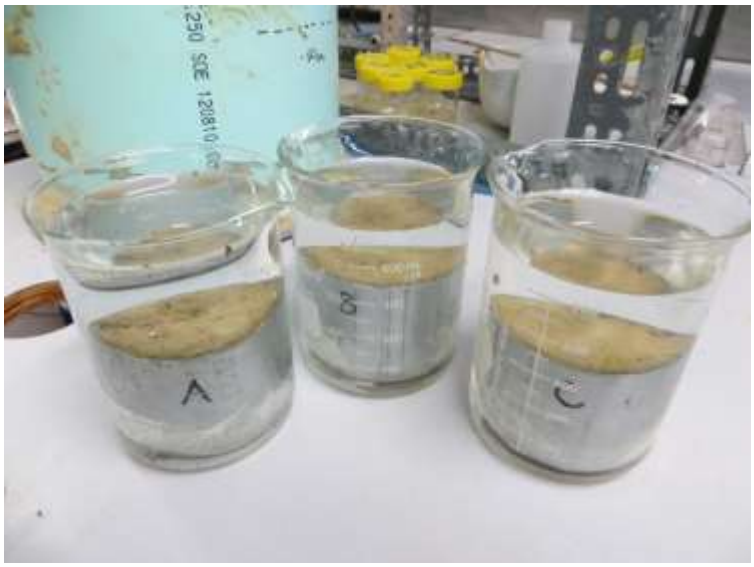

Figure 29. Submersion of porosity columns under deionized water.

9) After 24 hours has past, gently pick up the soil-mould and check the bottom parafilm to see if the soil is fully saturated at the bottom. If the soil is not fully saturated, put the soil-mould back in the water bucket for another 24 hours. Repeat until the soil is fully saturated through in the mould. It is important to minimize handling of the saturated soil-mould sample, to minimize soil loss.
10) Once the soil is fully saturated, remove the rubber band and the parafilm and wipe the outer surface of the mould dry with a piece of tissue paper.
11) Weight the saturated soil-mould.
12) Porosity can be determined using Equation 15, Equation 16, and Equation 17.

$$D = (\rho\ water * A) - (C - B)$$

[Equation 15]

A = volume of available space for soil, within the mould.

B = dry weight of in-situ soil only.

C = fully saturated weight of in-situ soil only.

D = weight of water occupying pore space within in-situ soil, g.

$$E = \frac{D}{\rho\ water}$$

[Equation 16]

E = volume of pores that water occupies within in-situ soil, m^3.

$$Porosity, \% = \frac{E}{A}$$

[Equation 17]

3.5. Leachate analysis methods

All collected, diluted, batched test and pore volume leachate were filtered through a disposable 0.45 micron syringe and filter before conducting the below experiments. Frozen or refrigerated samples were left in the lab for 3 hours prior to experimentation, this allowed for samples to reach room temperature before sampling.

3.5.1. Chemical oxygen demand (COD)

COD tests were conducted through a modified method, which closely follows that of HACH (2002)'s closed reflux meths system. The modification utilises a self-made COD high range digestion solution, and a created program in the spectrophotometer, DR2000. The program was created using absorbance values obtained from various concentrations of standards to create a standard curve. To ensure accuracy, duplicates of 600 mg/L COD standard is conducted with each batch of COD tests, to gauge accuracy. The range of tested standards during CoD batch tests were 608-655, over the standard 600 mg/L standard in all cases. CoD values can be affected by some experimental inconsistencies, explained further in the section 5. A copy of the standard curve used is appended in Appendix B.

3.5.2. Ammonia

Nitrogen, ammonia tests were conducted according to HACH (2002)'s Method 10031. The high range salicylate method measures ammonia concentration within 0.4-50.0 mg/L of NH_3-N. All samples were measured off a blank sample of de-ionised water (0 mg/L of NH_3-N). 3.819 mg/L ammonium chloride was used to make 1000 mg/L NH_3-N quality control (Q.C.) test solutions. Conducted tests are usually accurate to ± 0.5 mg/L if QA/QC is sufficient.

3.5.3. Nitrate

Nitrogen, nitrate tests were conducted according to HACH (2002)'s Method 8039. The cadmium reduction method measures nitrate concentration within 0.3-30.0 mg/L of NO_3^--N. All samples were measured off a blank sample of de-ionised water (0 mg/L of NO_3^--N). 0.722 mg/L potassium nitrate was used to make 1000 mg/L NO_3^--N Q.C. test solutions. Conducted tests are usually accurate to ± 0.5 mg/L if QA/QC is sufficient.

3.5.4. Total Nitrogen

Total nitrogen tests were conducted according to HACH (2002)'s Method 10072. The high range persulfate digestion method measures total nitrogen concentration within 10-150 mg/L of N. All samples were measured off a blank sample of de-ionised water (0 mg/L of Total-N). 14.0046 mg/L ammonium sulphate was used to make 1000 mg/L total nitrogen Q.C. test solutions. Conducted tests are usually accurate to ± 0.5 mg/L if QA/QC is sufficient.

3.5.5. pH

pH of samples was measured using EDT instruments microprocessor pH meter (Model #: RE 357-Tx). The instrument was calibrated with pH 4, 7 and 10 Scharlau buffer calibration solution each time before use. pH values were taken after 10 seconds of submersion of the temperature and pH probes into sample solutions, which was the estimated time for pH values to stabilize. Once pH values have stabilized, conducted tests are usually accurate to ± 0.02 pH if QA/QC is sufficient.

3.5.6. Conductivity

Conductivity of samples was measured using an YSI salinity conductivity temperature meter (Model #: 30-10 FT). The instrument was calibrated with 0.01M KCL conductivity standard at 1412 µS/cm at 25 °C each time before use. Conductivity values taken were displayed in µS/cm, already adjusted to 21°C; conductivity values were taken after 10 seconds of submersion of the conductivity probe into sample solutions, which was the estimated time for conductivity values to stabilize. Conducted tests are usually accurate to ± 50 µS/cm if QA/QC is sufficient.

3.5.7. Hills Laboratory Soil Analysis Methods

Soil samples were sent away for external analysis at Hills Laboratory, Hamilton. Table 6 shows a list of samples sent away for analysis, along with the parameters analysed, and methods used. Hills laboratory did not comment on accuracy obtained from these results.

Table 6. Soil samples sent to Hills for analysis and parameters analysed.

Kate Valley soil samples sent for analysis	Soil parameters analysed at Hills Laboratory	Method
0 – 200 mm soil depth	pH	1:2 (v.v) soil:water slurry followed by potentiometric determination of pH
200 – 400 mm soil depth	Olsen Phosphorus	Olsen extraction followed by molybdenum blue colorimetry
400 – 600 mm soil depth	Potassium	1M neutral ammonium acetate extraction followed by ICP-OES
	Calcium	1M neutral ammonium acetate extraction followed by ICP-OES
	Magnesium	1M neutral ammonium acetate extraction followed by ICP-OES
	Sodium	1M neutral ammonium acetate extraction followed by ICP-OES
	Cation exchange capacity	Summation of extractable cations (K, Ca, Mg, Na) and extractable acidity
	Total base saturation	Calculation from extractable cations and cation exchange capacity.
	Volume weight	The weight/volume ratio of dried, ground soil
	Organic matter	Organic matter is 1.72 * total carbon
	Total carbon	Dumas combustion
	Total nitrogen	Dumas combustion

3.6. Hills Laboratory Leachate Analysis Methods

Leachate and column pore volume samples were sent away for external analysis at Hills Laboratory, Hamilton. Table 7 shows a list of samples sent away for analysis, along with the parameters analysed. Hills laboratory did not comment on accuracy obtained from these results.

Table 7. Leachate samples sent to Hills for analysis and parameters analysed.

Leachate samples sent for analysis	**Leachate parameters analysed at Hills Laboratory**	**Method**
Raw leachate	Total Kjeldahl nitrogen	Total Kjeldahl digestion, phenol/hypochlorite colorimetry. Descrete analyser. APHA 4500-N_{org} D. (modified) 4500 NH_3 F (modified) 21st ed. 2005.
Pore volume from 10x column, Day 46	Total nitrogen	Calculation: TKN + Nitrate-N + Nitrite-N
Pore volume from 2x column, Day 26	Total ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete analyser. (NH_4-N = NH_4-N + NH_3-N). APHA 4500-NH_3 F (modified from manual analysis) 21st ed. 2005
	Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) –NO2N
	Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3-I 21st ed. 2005.
	Total organic nitrogen	Calculation: TKN – NH_4-N

4. Soil analysis results

4.1. Soil sieve results

Soil sieving was conducted on disturbed soil samples collected from Kate Valley on 17 April 2012. The method used to select and sieve soils is described in section 3.4.1.

500 g of soil was weighed out for each soil depth of 0 cm – 20 cm, 20 cm – 40 cm, and 40 cm – 60 cm soil excavation depths. The sieves seizes used were >0.84mm, 0.840mm > x > 0.60 mm, 0.60 > x > 0.187 mm, and <0.187 mm.

The results in Table 8 show that soil from the 20 cm – 40 cm soil depth category had the highest amount of soil more than 0.840 mm in size, however, it was noted that chunks of soil no bigger than 3 mm – 4 mm in diameter were left in the top layer of the sieve; had external force been applied to break these apart, some soil may have been sieved through. Soil particle size > 0.840 predominates in the upper soil layers 0-20 cm and 20-40 cm, 220.51 g and 224.61 g respectively; 40 – 60 cm depth soil had the lowest amount at 172.33 g. The weight of fine soils (0 mm – 0.6 mm in size), increases as soil depth increases; the opposite of larger soil particles 0.6 – 0.84 mm, and larger.

Based on Transwaste Canterbury (2002)'s soil classification, soils in the 0-20cm depth consisted mostly of coarse sand at 62.08%, 35.12% as medium sand and 1.67% as fine sands/silts.

Soils of 20-40 cm depth had 58.25% of coarse sand, relatively similar to that of 0-20cm layer. Medium sand in the 20-40cm layer was sieved at 39.11%, around 4% more than the upper 0-20cm layer. Fine-sands/silt content of 20-40cm was sieved as 2.9%, almost double that of 0-20cm layer.

Weight of coarse sand continues to decrease in sieved layer 40-60cm with 47.94%. This layer had the highest amount of medium-sands at 46.61%, and also fine-sands/silts at 3.47%.

Table 8. Soil particle size analysis for samples collected on 17 April 2012.

	0-20cm	20-40cm	40-60cm
Original Weight, g	500.01	500.08	500.00
> 0.840mm, g/%	220.15 / 44.03	224.58 / 44.91	172.35 / 34.47
0.840>x>0.60mm, g/%	90.25 / 18.05	66.71 / 13.34	67.35 / 13.47
0.60>x>0.187mm, g/%	175.60 / 35.12	195.58 / 39.11	233.05 / 46.61

< 0.187 mm, g/%	8.35 / 1.67	14.50 / 2.90	17.35 / 3.47

Comparing the sampled data from Table 8 along with Table 1 (Transwaste Canterbury, 2002) sieve analysis data of soil extracted from 3-4m depth; amount of coarse sand material may indicate a reduction to 0. Medium-sand will also reduce to around 9% at 3-4m depth, from an initial averaged of 40.28% in the 0-60 cm layer. Fine clay particles <0.002 mm in size will start appearing at 3-4m depths, comprising of around 9% of total soil composition. It is noted that the surface of Greenwood formation slopes into the ground, so depending on where samples are taken, soil profile depths can be expected to vary.

4.2. Soil parameter (Hills Laboratory) results

3 soil samples of varying depth into the ground (0-20cm, 20-40cm, 40-60cm) were collected on 14 June 2013 and sent to Hills Laboratory for analysis. The parameters tested include pH, phosphorus, K, Ca, Mg, Na, CEC, saturation, organic matter, total carbon and total nitrogen. A summary of methods used for these tests can be found in the Hills Laboratory analysis report Table 6. Tested parameter values are presented below in Table 9.

Table 9. Kate Valley soil analysis by Hills laboratory of different levels.

	KCS001 (0-20cm)	KCS002 (20-40cm)	KCS003 (40-60cm)
pH	8	8.3	8.3
Olsen Phosphorus, mg/L	7	8	9
Potassium, me/100g	0.12	0.13	0.12
Calcium, me/100g	8.7	12.1	11.7
Magnesium, me/100g	1.08	1.56	1.42
Sodium, me/100g	0.07	0.16	0.2
CEC, me/100g	10	14	13
Total Base Saturation, %	100	100	100
Volume Weight, g/ml	1.22	1.21	1.23
Organic Matter, %	0.5	0.6	0.5
Total Carbon, %	0.3	0.3	0.3
Total Nitrogen, %	<0.04	0.04	<0.04

The pH of the existing Kate Valley soil is basic at pH 8 – 8.3 through all layers; with no existing issues with metal mobility inherent with low soil pH.

Phosphorus increases with depth through the analysed depth of 0-50cm, steadily climbing by 1 mg/L every 20cm increment of depth. All levels of phosphorus currently exist in levels below any limits of concern.

Base cations such as Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} contribute towards cation exchange capacities of soils. CEC is also known to vary with the amount of clay content, type of clay, soil pH and amount of organic matter. Sand has very low CEC (usually less than 2meq/100 g). van der Perk (2006) reports typical CEC values of clay minerals kaolinite around 1-10 meq/100 g, illite 20-40 meq/100 g, montmorillonite 80-120 meq/100 g and vermiculite 120-150 meq/100 g; illustrating the strong influence of clay type on soil CEC. Reported CEC values of 0-20cm soil is moderately high at 10 meq/100g, this may be due to the quantity of organic constituents in this later. CEC was higher in 20-40cm and 40-60cm soils of 14 and 13 meq/100g respectively. Increases from 0-20cm soil is likely due to higher clay content in deeper layers, and high Ca^{+} in soil.

Organic matter of the soil exists throughout each analysed layer ranging between 0.5-0.6 %. This is quite low especially for the top layer of soil which would expect to be much higher than the deeper layers, due to its proximity to the vegetative surface of the soil.

Total carbon of the soil was low at 0.3 % throughout all layers of tested soil.

4.3. Volatile solids test results

Volatile solids test was conducted on 30 January 2013, using soil collected from 5 October 2012. Experimental procedure follows that outlined in section 3.4.2. The depths of soil tested were 0-20cm, 20-40cm and 40-60cm. Duplicates were conducted for each soil layer, and the results are shown below in Table 10.

Table 10. Duplicate volatile solids test results for 3 depths of Kate Valley soils.

Soil Type, cm	[B] Cup Weight (g)	[A] Soil & Cup Weight (g)	[D] Final Weight (after Burn) (g)	% Volatile Solids	Average Volatile Solid, %
0-20	38.4948	60.332	59.5284	3.6799	4.3228
0-20	37.7705	58.3942	57.3701	4.9656	
20-40	39.5816	64.2751	63.2756	4.0476	4.1163
20-40	38.2533	61.8615	60.8735	4.1849	

40-60	37.599	61.1542	60.3538	3.3979	3.3370
40-60	38.8466	62.3249	61.5557	3.2762	

Average percent of volatile solids in each layer decreased as depth progressed, starting at 4.3% to 4.1 % to 3.3 % for 0-20cm, 20-40cm and 40-60cm depths respectively. Values obtained for percent volatile solids in 20-40cm and 40-60cm depths were relatively consistent, with only 0.1% difference between duplicate samples for 20-40cm and 40-60cm depths respectively. The percent difference between duplicate values for 0-20cm layer was much larger at 1.3 %. This can be explained by large root material in soil mixture, when compared to the sample weight used for combustion (around 38 g each test). One selection of 0-20cm topsoil mixture could have been skewed by the inclusion of long or thick roots during the measurement stage.

4.4. Porosity test results

Porosity test was conducted on 2 July 2013, using soil collected from Kate Valley on 14th June 2013. Table 11 below shows the sampled porosity (% of pores), following the method detailed in section 3.4.3.

Table 11. Porosity (%) results for Kate Valley soils from 3 depths.

	porosity (%)		
	Topsoil 0-10cm Depth	10-25cm Depth	25-40cm Depth
	36.21	37.67	41.63
	34.98	-	43.78
	34.25	35.66	44.27
Average	35.15	36.66	43.23

Triplicate tests were conducted for each soil of the 3 tested soil depths. 10-25cm depth tests only had duplicate results as soil's in-situ structure of the third porosity test experiment was compromised during excavation. The data obtained for topsoil closely relates to Transwaste Canterbury (2001)'s reported value of 34% porosity, for the Greenwood formation.

Experimental difficulties which affected the accuracy of the results mainly existed through soil loss. Soil loss occurred in the saturation phase of the porosity experiment, during

submersion and extraction of soil moulds from water, as dislodged soil particles separated from the soil mould from currents induced by equipment entering the water body to extract the soil mould. Unaccounted soil loss will result in overestimation of porosity, as these final un-weighed soil particles will be calculated as weight of voids when saturated weights are subtracted from dry soil weights for water capacity; crucial for calculating porosity space. This effect was minimized by taking care with slow and steady extraction of the soil mould with handled equipment.

5. Batch test results and discussion

This chapter analyses the results obtained from a series of batch tests, conducted on various Kate valley leachate dilutions and soil sample mixtures. Table 12 below shows the combination of batch tests conducted, along with sample collection dates, type of batch liquid used and type of batch soil. Full set of results are located in Appendix C.

Table 12. Analysis and tests conducted for batch test experiments.

Batch Phase/Sample collection date	Samples Collected	Tests Conducted	Analysis conducted
Phase I (17-Apr-12)	Landfill leachate and disturbed soil samples.	0-20 cm, 20-40 cm, and 40-60 cm soil with 5x and 50x raw leachate dilution	pH, conductivity, CoD, ammonia, nitrate, total nitrogen.
Phase II (5-Oct-12)	Disturbed soil samples to a depth of 1m (with soil auger) and landfill leachate	Duplicate batch test of 0-20 cm, 20-40 cm, and 40-60 cm soil depth with 5x, 20x, and 50x raw leachate.	pH, conductivity, CoD, ammonia, nitrate, total nitrogen.
Phase III (14-Jun-13)	landfill leachate and *in-situ soil samples.	0-20 cm, 20-40 cm, and 40-60 cm soil with 3x, 4x, 5x, 6x, 8x, 20x, and 35x leachate	ammonia, CoD

***Discussed further in section 6.**

Results discussed below were based on batch experimental conditions of 30 g of respective soil and 70 ml of respective batch liquid. Agitation period was set at 24 hours for all batch tests. Samples were stored in refrigeration (4°C) until sampling was conducted at room temperature (20°C); as previously explained in experimental method and sampling in section 3.3.1. After the kinetic batch tests, samples were allowed to settle for 2 hours and subsequently filtered before analysis.

Throughout the 3 batch test phases, various combinations of liquid phase (raw leachate and control dilutions) were paired with the 3 soil phases (soil depths 0-20 cm, 20-40 cm, 40-60cm). The liquid phases tested in the batch test experiments include: raw leachate, control (de-ionized water), 3x, 4x, 5x, 6x, 8x, 10x, 20x, 35x and 50x raw leachate dilutions. These results are expressed as initial concentrations, and can be found in:

Appendix C1: Sampled initial pH, COD and conductivity values in leachate.

Appendix C2: Calculated initial and sampled equilibrium pH, EC and COD.

Appendix C3: Sampled initial ammonia and total nitrogen values in leachate.
Appendix C4: Calculated initial and sampled equilibrium ammonia, nitrate and total nitrogen.

Data obtained from the batch tests were not used extensively as reportable values, rather as an early indication of what adsorptive values may be. The Phase I batch tests served more as a practice exercise for the student to familiarise with the methods and experimental equipment and procedures of obtaining reliable and reportable data.

Although the focus of this research is on nitrogen behaviour in the sub-surface soil, the behaviour of the other parameters is of interest because it provides an overall picture for what can be expected from land application of leachate.

5.1. pH behaviour

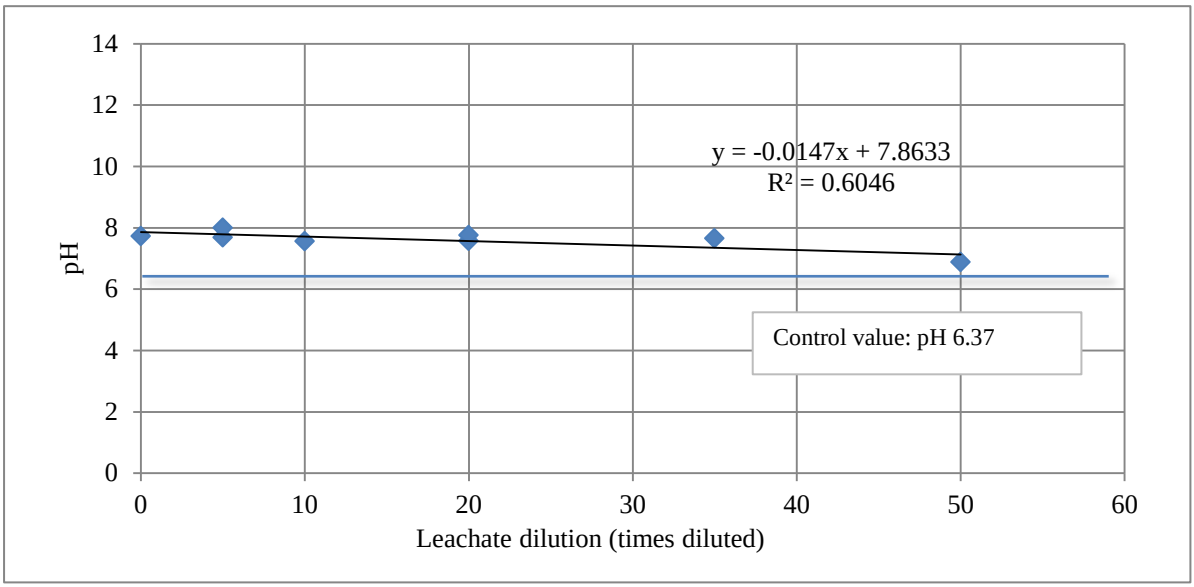

Figure 30. Initial pH values of various raw leachate ratio solutions.

The reported pH values of de-ionized water, raw leachate and their various ratios in solutions were tested and reported in Figure 30. Data values for these experiments can be found in Appendix C1. Values of pH in between sampled dilution ratios can be estimated using the linear relationship equation shown in Figure 30, which applies to dilutions from 0 (raw leachate) to 50 times dilution. The tested pH of de-ionized water was pH 6.37.

When examining the control cases, the batch solution decreased from an initial pH of 6.37 to an average of 4.62, 4.82 and 5.02, for 0-20 cm, 20-40 cm, and 40-60 cm soil respectively (i.e.

increasing soil depth increments). These values were largely acidic, with the most severe case being topsoil, possible explanation are likely due to experimental errors on the student's part of forgetting to calibrate the pH meter before sampling takes place.

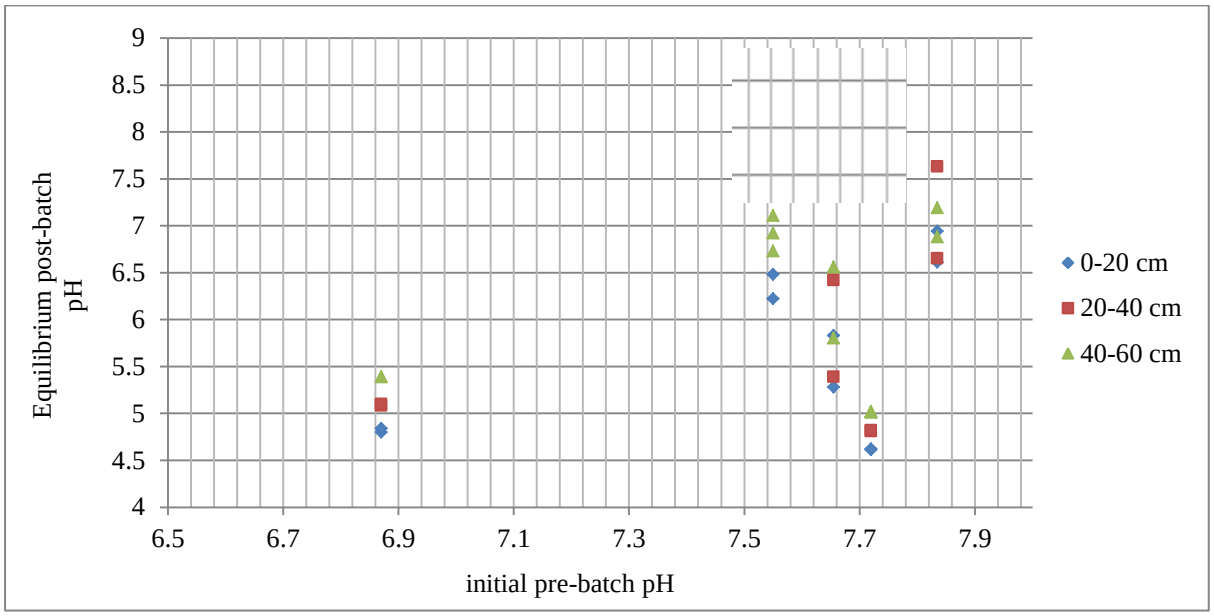

Figure 31. Pre-batch vs. equilibrium pH for all soils tested.

Leachate dilutions used in batch tests were converted to initial pre-batch pH values and plotted with equilibrium post-batch pH, the results are shown above in Figure 31, reported from Appendix C2.

From Figure 31, there appears to be no significant influence of soil type on the pH of batched solution. On average, soil from the 40-60 cm soil layer has shown to have higher soil pH values than its above layers, however, the differences in pH between soil layers were not large enough to be of note.

Batch solution and amount of dilution applied to each batch test has a larger influence on final equilibrium pH of batch solutions. This is understandable as the pH of de-ionized water would overwhelm that of raw leachate; taking into consideration that pH of equilibrium concentrations is determined from hydrogen ion molarity, rather than the sums of dilute volume. In batch cases where there is less raw leachate dilution, equilibrium pH values are closer to that of raw leachate at pH 7.72; and vice versa for high dilution being closer to control pH of 6.37.

For the batch tests where pH tested very basic (pH 8-9), it is possible that some ammonia content volatilized. The results may have been affected by the duration in which the samples

were exposed to the air, before, during and after sampling. Periods of air exposure before and after sample analysis include the air space within storage containers which were not filled with leachate; during sampling, air contact was introduced through the unfilled space of the batch container. Duration between sample batch tests and analysis did not exceed 2 weeks.

5.2. Conductivity behaviour

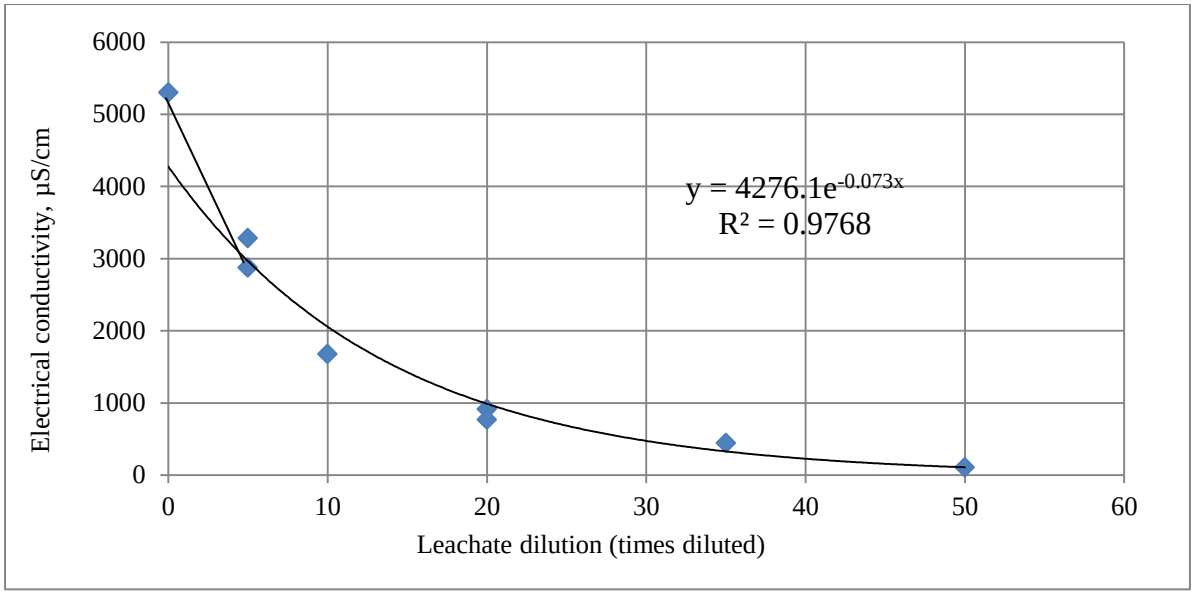

Figure 32. Initial conductivity values of various raw leachate ratio solutions.

Figure 32 shows sampled electrical conductivity values of raw leachate with increasing dilution. The data points used to plot Figure 32 can be found in Appendix C, and were based off of experimental measurements following method section 3.5.6. The exponential equation shown in Figure 32 can be used to estimate electrical conductivity values between dilution ratios of 5-50 times raw leachate dilution. The exponential relationship does not accurately describe behaviour between raw leachate (5300 µS/cm) and 5x (average of 3077 µS/cm), thus a linear relationship will be used to estimate concentrations between 0-5x dilution.

Initial pre-batch conductivity values was plotted against equilibrium conductivity values for each soil layer in Figure 33-35, using data reported in Appendix C. Linear relationships were drawn using Microsoft Word's linear "Trendline" tool.

Results show that soil initially increased equilibrium batch liquid electrical conductivity, from an initial 1.9 µS/cm to average values of 402 µS/cm, 410 µS/cm and 438 µS/cm for respective increasing soil depth increments. Based on these averaged values of the soil types tested, deeper soils have a higher capacity to release electrical conductivity gathered on the soil into de-ionised water solution during batch test.

Conductivity of the control and topsoil case averaged 151.75 µS/cm. A large portion of this conductivity is speculated to have "washed" from the soil. The same result was observed for control and 40-60cm soil depth, however, these values averaged higher than topsoil at 286.6

µS/cm. This may be explained from topsoil being first contact with precipitation or runoff activity, thus soil in layers closer to the surface experiences more "soil washing". Conductivity is infiltrated through the soil and accumulates at soil depth.

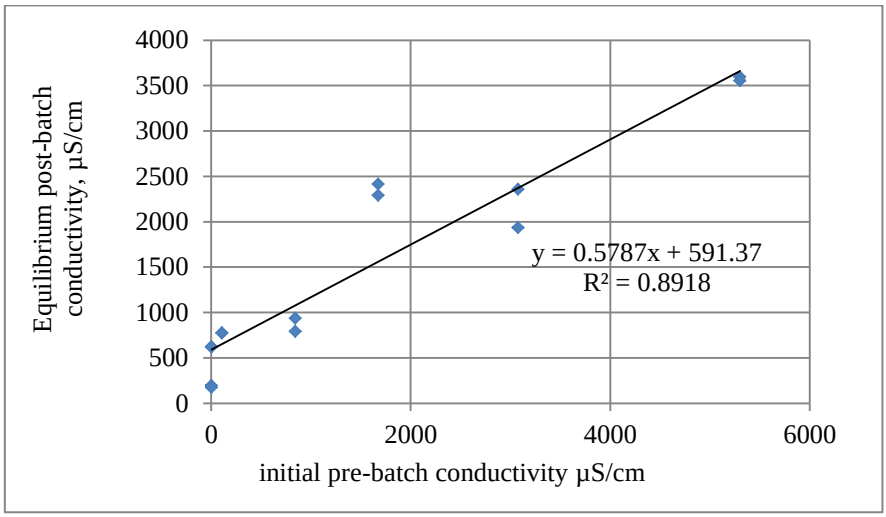

Figure 33. Pre-batch vs. equilibrium conductivity for 0-20 cm soil.

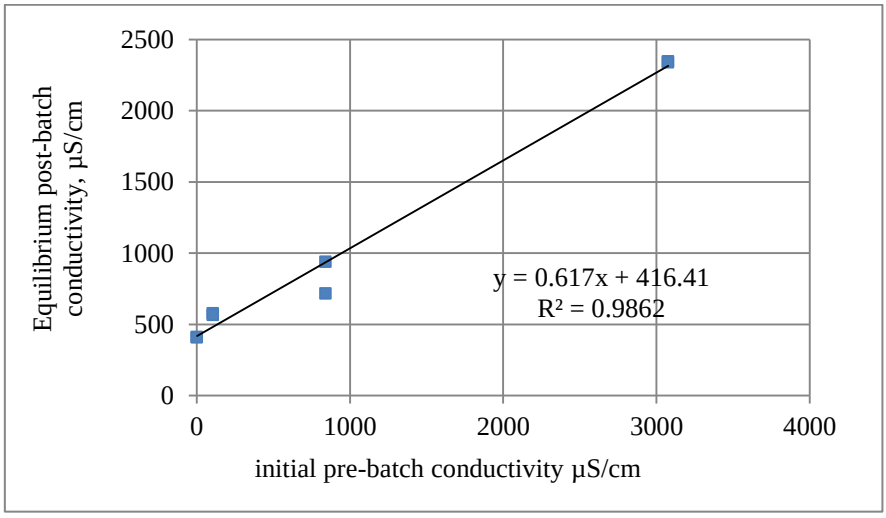

Figure 34. Pre-batch vs. equilibrium conductivity for 20-40 cm soil.

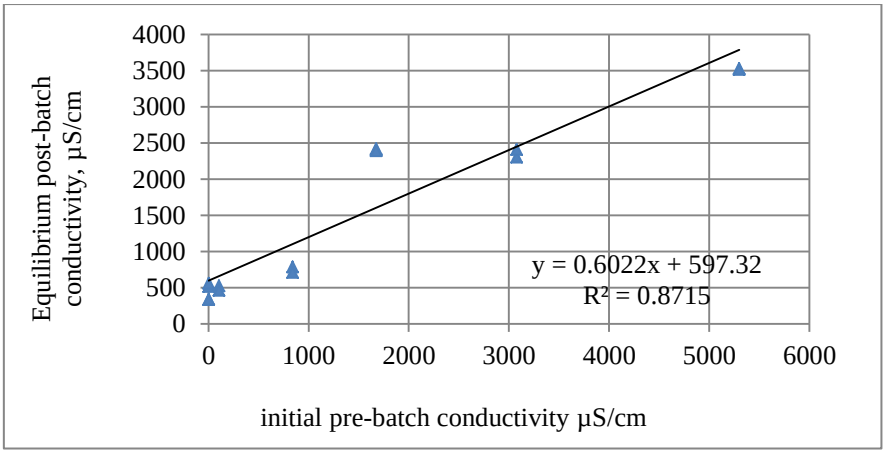

Figure 35. Pre-batch vs. equilibrium conductivity for 40-60 cm soil.

Adsorption ability of soil layers can be described by the slope of fitted trend lines in Figure 33-35, as steeper slopes signifies a higher capacity for the soil to adsorb electrical conductivity from the batch solution. However, between all soil layers, the slope remains relatively similar, ranging from 0.5787-0.617, this shows that between leachate strengths tested, the adsorbance capacity can be loosely described with an increasing linear relationship. 20-40 cm soil layer exhibited the best conductivity adsorbance with a slope of 0.617, followed by 0.6022 for 40-60 cm soil, and the least adsorbance of 0.5787 for 0-20 cm soil layer. Trendlines were drawn based on many sample points, with only 1 high leachate strength sample point used for plot, this has a large effect on how trendlines are fitted.

5.3. COD behaviour

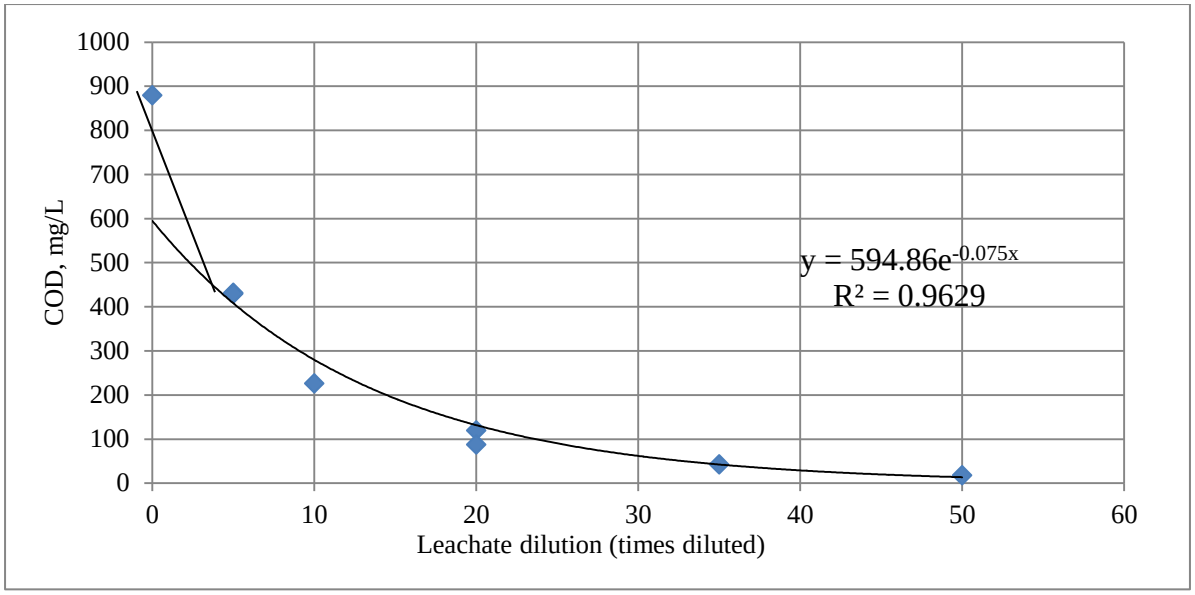

Figure 36. Initial COD values of various raw leachate ratio solutions.

Figure 36 plots sampled COD levels in various leachate dilutions. The data points used to plot Figure 36 can be found in Appendix C, and were based off of experimental measurements following method section 3.5.1. The exponential relationship shown in Figure 36 can be used to calculate initial COD values for raw leachate dilutions from 5-50 times dilution. In the same manner as conductivity, this relationship does not estimate behaviour well within the 0-5 times dilution range, thus linear interpolation will be used.

Initially measured pre-batch COD values is plotted against equilibrium COD values in Figure 36, for all soil layers using reported experimental values shown in Appendix C. It can be seen that there is large scatter in the presented results, underlining significant interferences in detection of COD during these batch experiments, which are discussed further later on.

Trends that can be observed through all soil layers is the apparent phenomena of soil giving off COD in the sampled equilibrium solutions, as shown in Figure 37. From observations, it can be seen that for the tests conducted, the type of soil used has a much higher effect on mg of COD given off/mg of soil than the leachate dilution used. Topsoil gave off the most COD between the 3 soils tested, followed by 20-40cm and 40-60cm in all leachate dilution cases. This may have been due to the high amount of organic content of the upper soil layers, due to root material and proximity to topsoil, where more organic exchange occurs, than lower deeper soils.

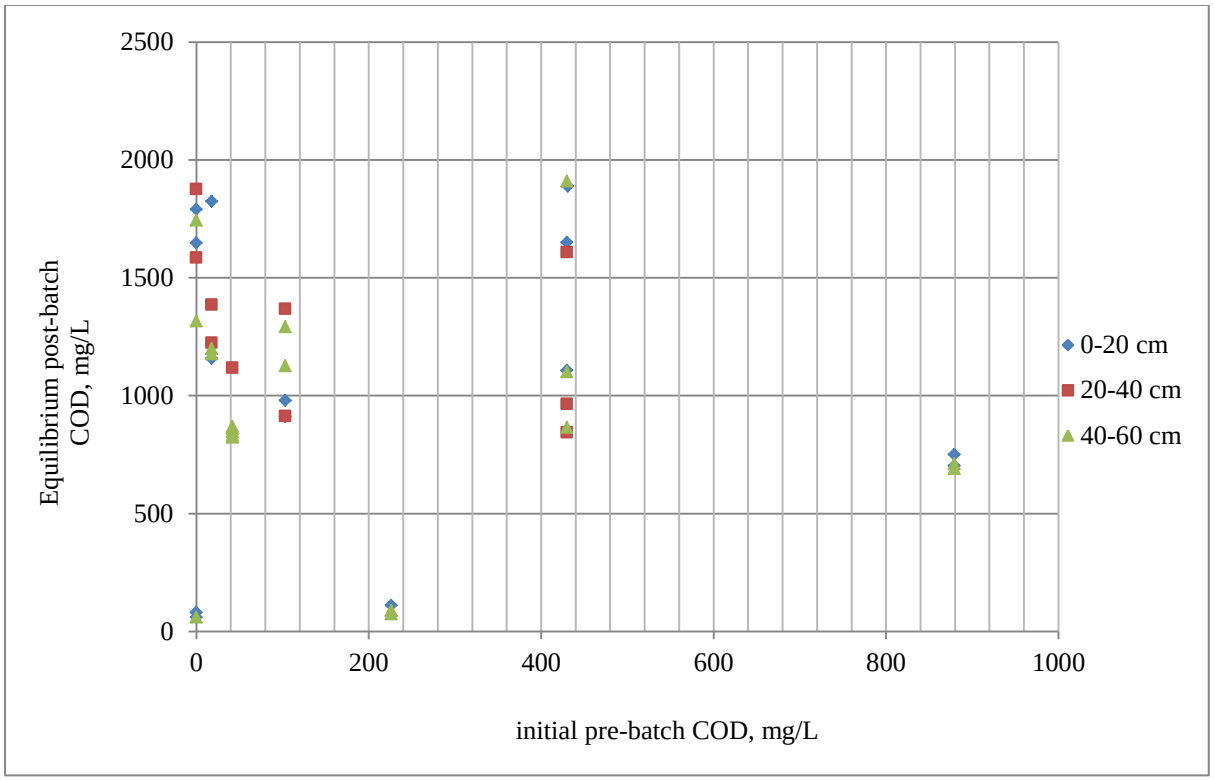

Figure 37. Pre-batch vs. equilibrium COD for all soil layers.

This is examined further in Figure 38, where COD values were plotted based on amount of COD given off /mg of soil; calculated following section 2.5.1.

Figure 38 shows that between all soils, the amount of COD given off decreases as initial pre-batch COD gets closer to raw leachate value of 879 mg/L. This can be explained by the raw leachate liquid phase being more saturated with organic content, thus having more potential for organics to kinetically adsorb onto available soil adsorption sites; conversely, when de-ionized water is used (control case), there are negligible organics available for kinetic adsorption, organic content initially adsorbed to soil sites are more likely to enter solution during batch kinetics, increasing the solution's COD. This effect will be more prominent in topsoil layer (0-20 cm) as more organic activity occur there, as depth increases, so does the capacity of soil releasing COD into solution. This can be observed in Figure 38, where on average 40-60 cm soil release less mg of COD/mg of soil (~ 0.0002 mg COD/mg soil) than 20-40 cm (~ 0.0025 mg COD/mg soil), and 20-40 cm soil releasing less mg of COD than 0-20 cm (~ 0.0030 mg COD/mg soil).

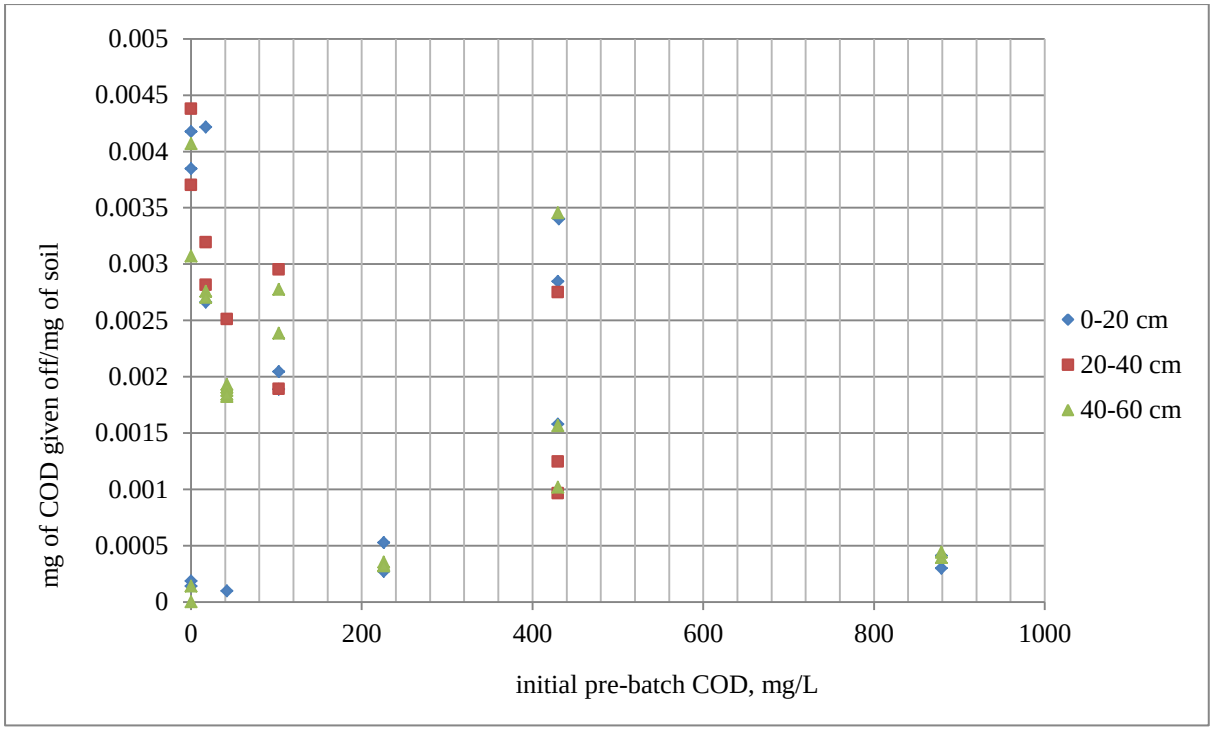

Figure 38. pre-batch COD concentration vs. mg of COD given off /mg of batched soil, for all soil layers.

Interpretation of the COD results for the batch tests is made difficult because of the limitations of the COD test. COD tests have been discussed by Kylefors et al. (2003) as inadequate as the sole measure of organic matter. In his study of "Accuracy of COD tests for landfill leachates", one finding shows that almost a third of COD values tested could have inorganic origins. COD tests can be poor measures of organic strength because many other substances can contribute towards COD values; including inorganic substances such as iron, sulphides, manganous manganese, ammonia nitrogen, nitrite and chlorides; with sulphides and iron (II) interfering most with COD measurements. Furthermore, many of these contaminants can exist in significant concentrations in landfill leachates.

5.4. Nitrogen behaviour

Ammonia and total nitrogen concentrations in raw leachate can be estimated using Figure 39 and 40 respectively. The data points used to plot Figure 39 and 40 can be found in Appendix C and were based off of experimental measurements following method section 3.5.2. and 3.5.4. The exponential relationship shown in each Figure can be used to calculate initial concentration values for raw leachate dilutions from 5-50 times; linear interpolation is used between 0-5 times dilution, as respective equations do not model values well in this region.

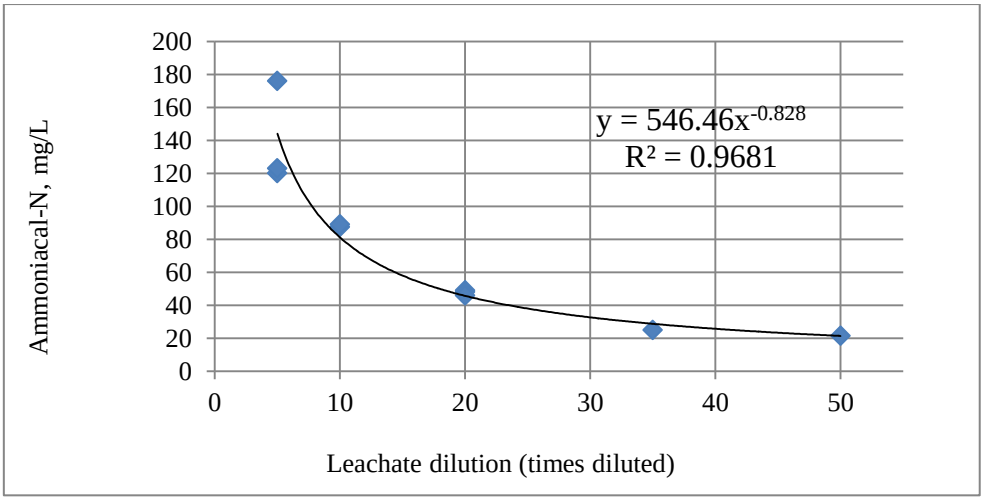

Figure 39. Initial ammonia values of various raw leachate ratio solutions.

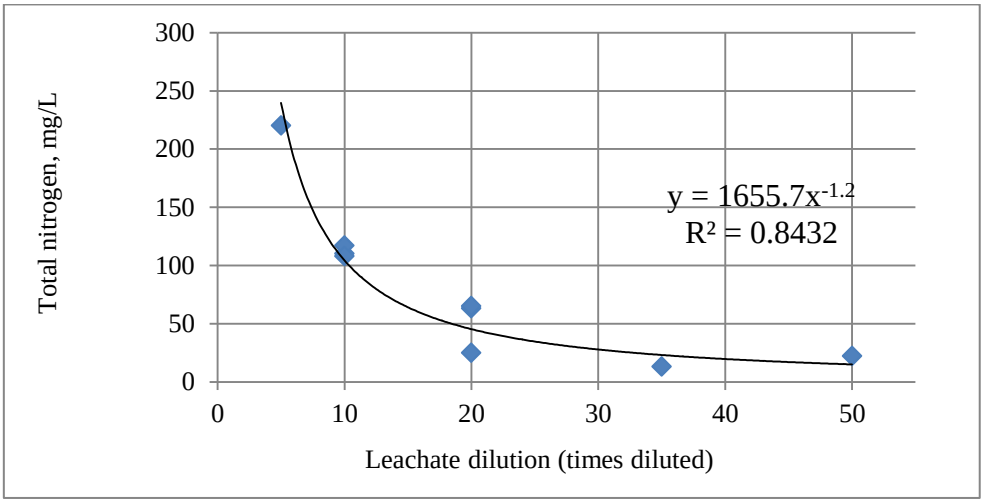

Figure 40. Initial total nitrogen values of various raw leachate ratio solutions.

Nitrate levels in raw leachate was sampled at 0.02 mg/L, which is negligible when compared to that of ammonia, subsequent dilutions of this would yield lower concentrations, thus they were not sampled extensively.

Figures 41-43 plots initial pre-batch ammonia with equilibrium ammonia concentrations (after batch experiment) for each increasing soil depths, respectively. Figure 44 plots pre-batch with equilibrium concentrations for total nitrogen, for all soil layers.

When soil was batched with de-ionized water, small amounts of NH_3-N was detected in equilibrium solution, namely an average value of 1.05 mg of NH_3-N/L in 0-20 cm topsoil and average of 0.3 mg of NH_3-N/L in 40-60 cm soil; although no control data was obtained for 20-40 cm soil, its NH_3-N level can be assumed to be negligible from the low levels detected in 0-20 cm and 40-60 cm batch samples. As the initial de-ionized water had no NH_3-N

content, the increase in NH_3-N in equilibrium solutions can be assumed to have originated from the batched soil, where ammonia content is "washed" from the soil into solution.

Nitrate concentration in soil was only sampled for 0-20 cm and 40-60 cm batch samples. 0-20 cm averaged 9.1 mg of NO_3^--N/L while 40-60 cm soil averaged higher at 18.05 mg of NO_3^--N/L. The 2 data points used to obtain the average concentration of nitrate in 40-60 cm soil should only be used indicatively, due to the low amount of batch samples conducted, and the values which make up this average were 30.3 and 5.8 mg of NO_3^--N/L.

Total nitrogen was not sampled in control cases, but can be assumed to be detected in slightly higher levels than ammonia, after taking into consideration of organic nitrogen, TKN, nitrates and nitrites.

Adsorptive behaviour of ammonia is examined with Figure 41-43. Best fit linear curve lines were fitted using Microsoft Word's "Trendline" function; linear equations and R^2 values are displayed on respective figures for each soil layer. The blue lines on Figure 41-43 denote the "1 vs. 1" adsorption threshold. Linear relationships following the line will represent no adsorption, where all the ammonia put into batched solutions sampled in equilibrium concentrations. Linear relationships with gradients less than the "1 vs. 1" line denotes adsorption, i.e. equilibrium concentration will be less than that of initial concentrations, since ammonia has adsorbed onto soil particles surfaces; likewise, linear gradients steeper than the "1 vs. 1" line denotes equilibrium concentrations higher than initial concentrations.

In the case of ammonia, all soil layers exhibit adsorptive behaviour of ammonia onto soil particle surfaces, the gradient of the soils are 0.8329, 0.8651 and 0.8751 respectively for 0-20 cm, 20-40 cm and 40-60 cm soil. These results would indicate 0-20 cm soil as most effective at reducing ammonia from initial concentrations with its linear slope of 0.8329, followed by 20-40 cm soil and 40-60 cm soil. However, adsorption cannot be solely responsible for the reduction of initial ammonia concentrations, as other processes such as nitrification, volatilization and microbial activity also contribute towards the various reduction mechanisms of ammonia concentrations from these batch tests.

Linear curves used to explain these results were also plotted from data points which, in some regions, lacked the sample points to form a definitive answer. These regions mostly exist in high concentration batch samples (>150 mg/L initial concentrations). High initial concentration batch tests were difficult to sample due to the need for extensive dilution in

equilibrium solutions, down to detectable range of experiment tests. High concentration leachate was also highly variable in colour and consistency; colour of raw leachate interfered with a lot of the sampling as they were mostly of photo-spectrometric detection methods, and the consistency of raw leachate was problematic as raw leachate was a combination of particulate matter and raw leachate solution, filtering of samples to maintain liquid consistency was decided against in pre-batch test due to the possibility of changing its nature and interaction with batch soil during experimentation.

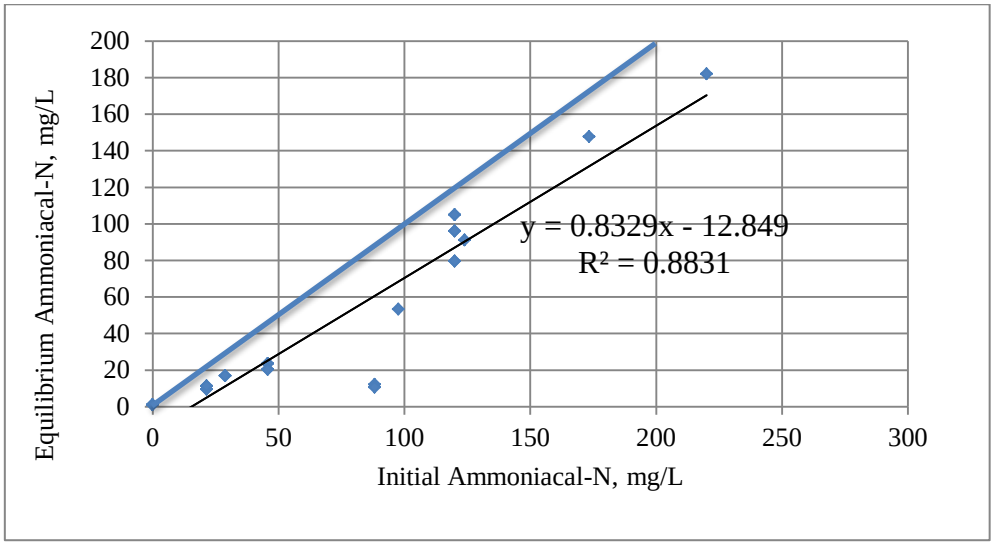

Figure 41. Initial vs. equilibrium ammonia concentrations for 0-20 cm batch soil.

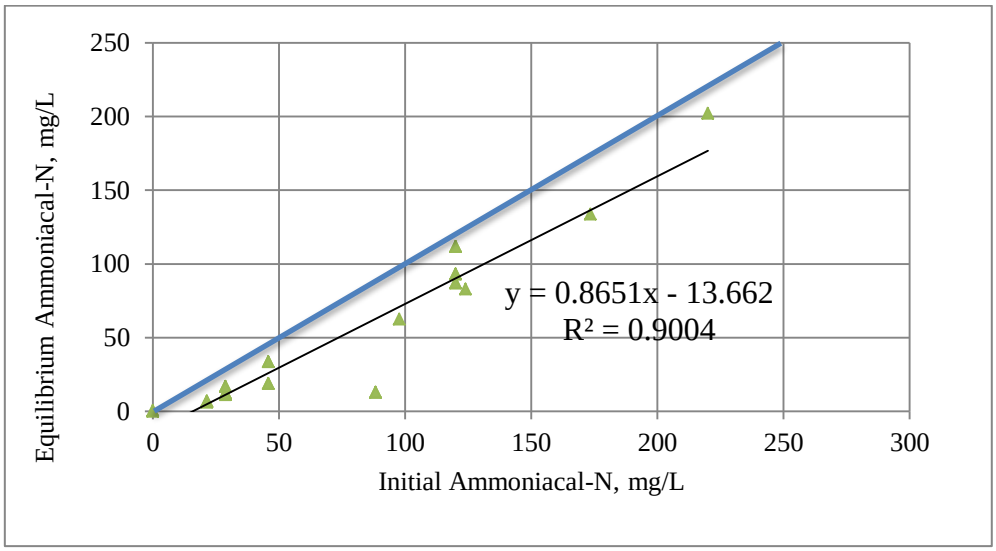

Figure 42. Initial vs. equilibrium ammonia concentrations for 20-40 cm batch soil.

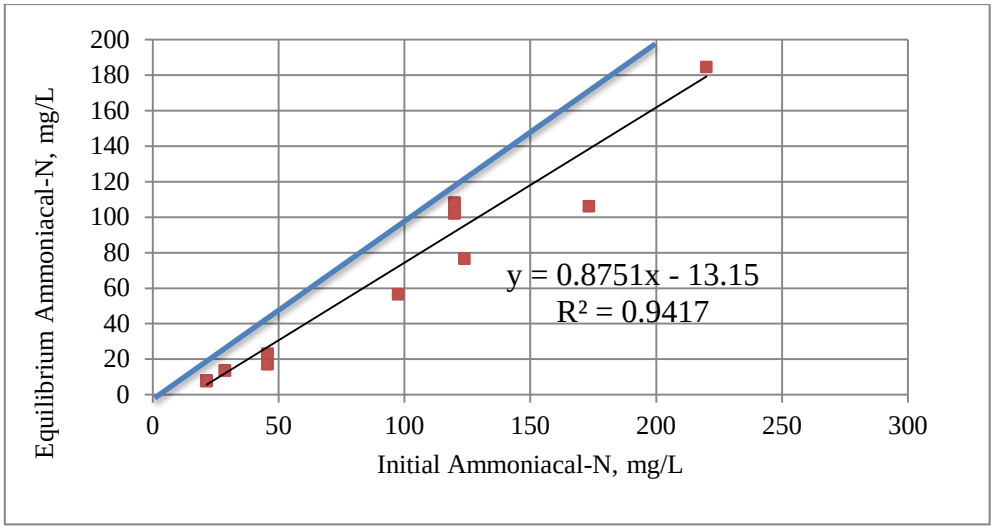

Figure 43. Initial vs. equilibrium ammonia concentrations for 40-60 cm batch soil.

From the examined results of Figure 41-43, the sampled ammonia range did not appear to have reached an upper adsorptive limit for ammonia, as most of the data results appeared to have conformed to a linear trend.

An "upper limit" to the adsorption of total nitrogen concentration may be indicated in Figure 44, however, this may be misleading due to the small amounts of total nitrogen tests performed on equilibrium solutions; results from initial 50 mg/L of total nitrogen tests may have reported higher than actual values, thus creating the illusion that the reported equilibrium concentration of 220 mg of total-N/L as "upper limit".

Given the relatively more extensive sampling of ammonia's linear adsorptive behaviour, and that total nitrogen should always be sampled more than ammonia concentrations, the assumption that total nitrogen was reported too high in initial concentrations ~50 mg of NO_3^--N/L is a more feasible explanation.

After batch tests, some nitrate levels were tested higher than ammonia levels. This shift in ammonia and nitrate levels may possibly be attributed to the nitrification process. High ammonia level in raw leachate is assumed to be due to ammonium's stability as a compound under methanogenic conditions (Burton & Watson-Craik, 1998).

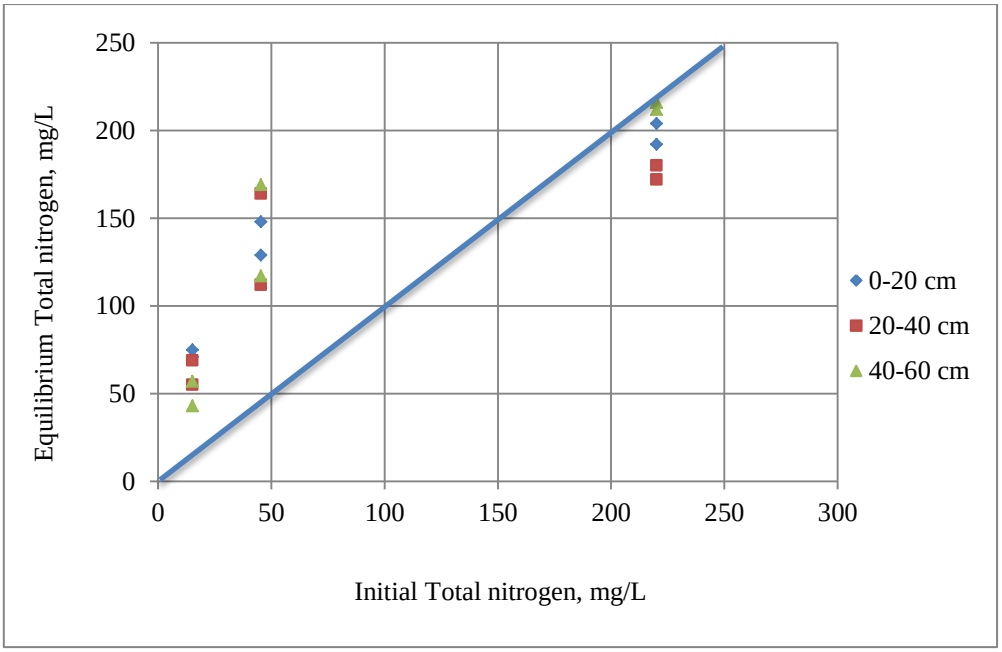

Figure 44. Initial vs. equilibrium total nitrogen concentrations for all batch soil.

From the sampled nitrogen results, ammonia was most extensive and informative in terms of forming relationships to determine partitioning coefficients and retardation factors to compare with that of column experiments, discussed later on in section 6.

Figures 45-47 plots ammonia equilibrium concentrations via mg of NH_3-N adsorbed/mg of soil basis for 0-20 cm, 20-40 cm, and 40-60 cm soil respectively (calculation method in section 2.5.1.). The orange line on Figures 45-47 show a hand-drawn linear relationship for these data points, these were drawn by the student and denotes an estimate of where linear adsorptive behaviour can be expressed. It is important to analyse adsorption data as it gives an indication to the soil adsorption and attenuation of contaminants. It also determines the number of pore volumes required to achieve breakthrough of a contaminant; it provides the necessary information for the determination of the retardation parameter for calculation contaminant transport (Yong et al., 1992).

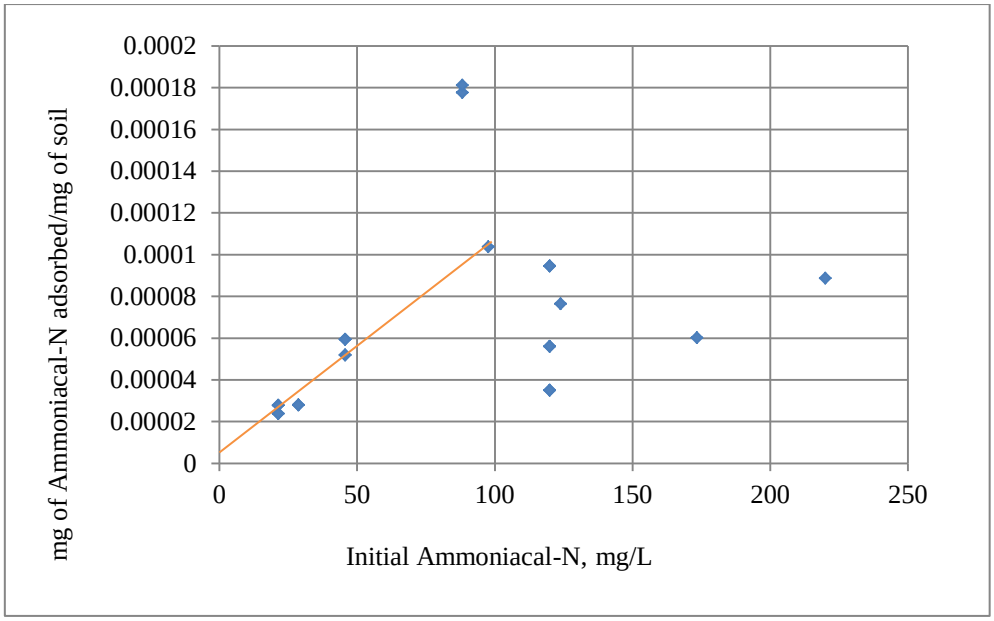

Figure 45. Adsorptive behaviour of ammonia on mg of leachate / mg of soil basis, for 0-20 cm soil.

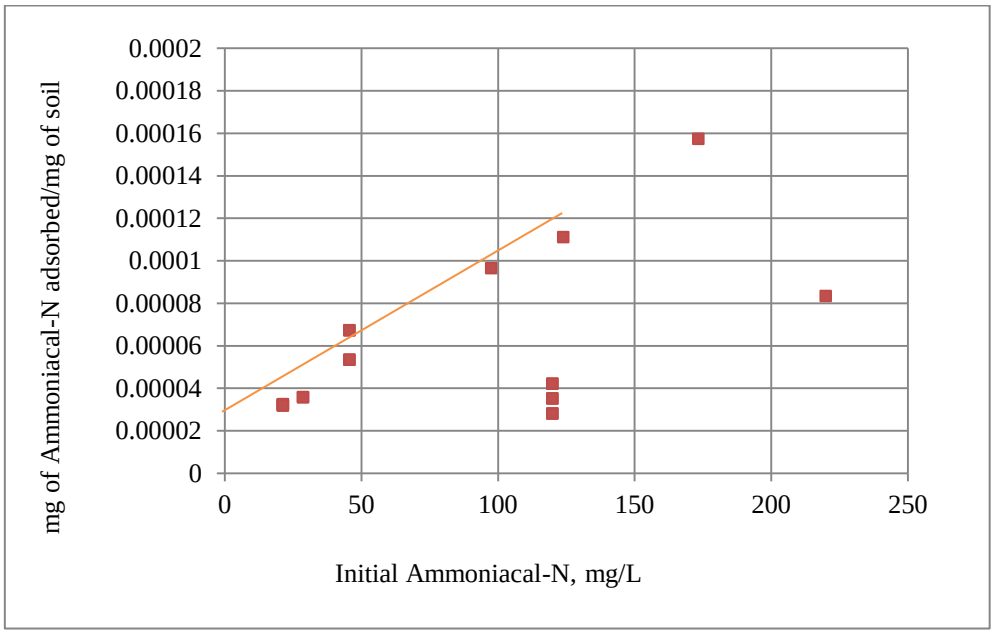

Figure 46. Adsorptive behaviour of ammonia on mg of leachate / mg of soil basis, for 20-40 cm soil.

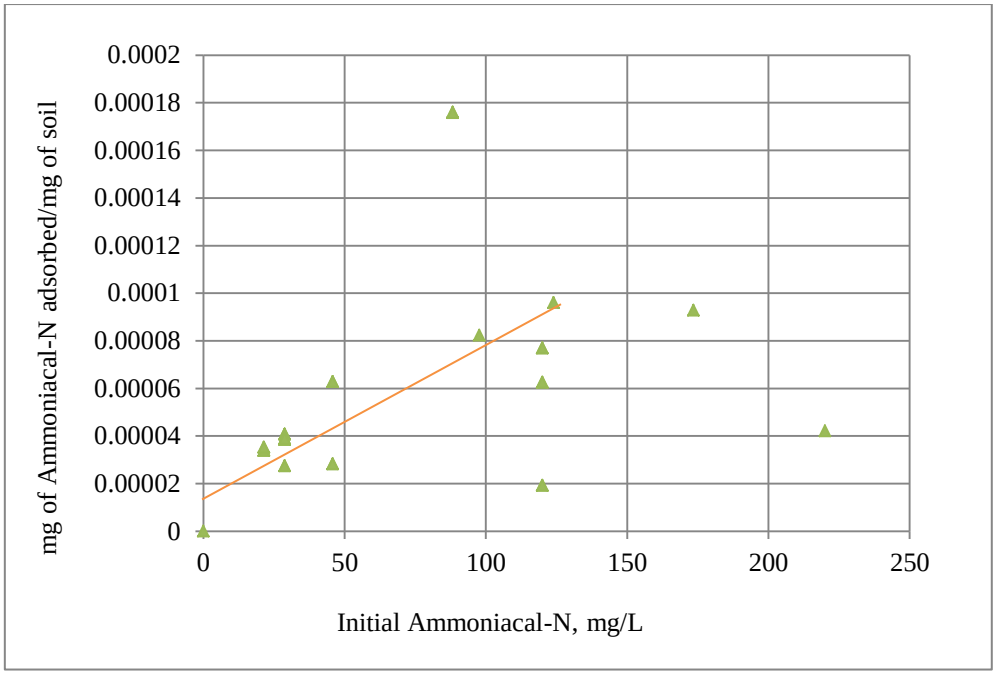

Figure 47. Adsorptive behaviour of ammonia on mg of leachate / mg of soil basis, for 40-60 cm soil.

Table 13 below contains K_d, and R values for each of the 3 soil types tested, obtained from batch test data. These values were obtained from interpretation of the gradient of the line in Figure 34-36. The unit of partitioning coefficient used is L/mg. K_d can be seen to decrease as soil depth increases (from 0.00000095 to 0.000064 L/mg). These results would suggest 0-20 cm is most effective at adsorption of ammonia concentrations than subsequently tested deeper soil layers, with the deepest 40-60 cm soil layer being most ineffective.

Retardation factor is calculated from the method detailed in section 2.5.1. Porosity values used were those sampled from section 4.4, bulk density value of 1780 kg/m^3 was used from reported dry bulk density for Greenwood formation (Transwaste Canterbury, 2002).

The R value results shown in Table 13 are all around the range of "3-9", which Weiner (2000) classifies as "mobile". Relative to each sampled soil layer, 0-20 cm soil layer would be have the least contaminant mobility due to its highest calculated R factor of 5.83; contaminants would have the most mobility in 40-60 cm soil due to its lowest R factor of 4.25.

Table 13. Summary of soil partitioning coefficient and retardation factor for each soil depth.

Soil Depth	Partitioning coefficient, K_d (L/mg)	Retardation Factor, R
0-20 cm	0.00000095	5.83
20-40 cm	0.00000072	4.66
40-60 cm	0.00000064	4.25

To verify the nitrogen balance, a set of nitrate, ammonia and total nitrogen tests were conducted in triplicate on the raw leachate samples, using soil from the 40-60cm layer along with 10x dilution of landfill leachate, the averaged results are shown below in Table 14.

Table 14. Nitrogen balance check, conducted on the 15th of June 2012.

	Nitrate (mg NO_3^--N/L)	**Ammonia (mg of NH_3-N/L)**	**Total Nitrogen (mg Total-N/L)**	**Nitrogen Balance Remainder mg/L**
Sample 1	21.5	13.9	24	-11.4
Sample 2	12.6	14.5	17	-10.1
Sample 3	25.5	8.9	16	-18.4

All 3 samples tested nitrates and ammonia in excess of total nitrogen, which is illogical as total nitrogen concentrations should cover that of ammonia, nitrate, organic nitrogen, TKN, and nitrites.

Reasons why nitrogen tests may have been in error may be due to the inexperienced nature of the student at the time. In the case of total nitrogen, testing involves quite a few extensive steps to complete, detailed in section 3.5.4.

Reasons why nitrate may have been tested so high may be due to experimental error where nitrate samples were blanked with de-ionized water, rather than a sample of leachate, as detailed in 3.5.3.

Other more general reasons for errors (besides from carelessness and inexperience) include: errors inherent from samples used. This includes the previously discussed problem of raw leachate colour, affecting results of photometric sampling employed to test nitrogen samples. All ammonia, total nitrogen, COD, and nitrate samples conducted by the student involved methods where spectrometric devices were used to detect contaminant levels, where colour may have a varying effect on accuracy between each test.

The introduction of oxygen into the sample throughout sample gathering, sample storage, and sample testing was not extensively minimized. As volatilisation could affect ammonia interactions after mixture with soil particles, it is important in future tests to consider the amount of airspace allowed during kinetic stages of batch tests.

Dilution of samples was often required to dilute equilibrium samples to within detection limits of the employed sampling methods. Careful selection and extraction of representative equilibrium samples was paramount in mixing with de-ionized water solutions, as extraction of unrepresented leachate samples could compound the dilution of leachate.

Experimental results obtained from batch tests were more coherent towards the later parts of batch test experiments (Figure 41-47), as sampled equilibrium values of ammonia and total nitrogen began to reveal trends and reported in logical values (e.g. ammonia levels less than total nitrogen). External sampling (Hills Laboratory) of equilibrium concentrations was not conducted for batch test experiments, thus comparison could not be drawn on accuracy between the student and Hills Laboratory. Samples of equilibrium pore volumes from column tests were sent for external analysis, thus discussion of coherence between sampled values can be discussed further on in section 6.

6. Column test results and discussion

Four in-situ soil monolith columns were extracted from Kate Valley on 14-Jun-13. These columns were for testing 2x raw leachate case (high-strength, column "E"), 10x raw leachate dilution case (medium-strength column "D"), a control column case (de-ionised water "F"), and bromide column sampling (KBr column).

Each column was irrigated at roughly 48 hour periods with 40 mm of respective irrigate (1520 ml), and pore volumes were collected at subsequently noted times after irrigation (data results in Appendix D).

Experimental sampling length for each column was variable; these were dependent on resources available, time constraints and results obtained. Column D was tested for 78 days; column E for 58 days; the control column for 17 days; and the bromide "KBr" column for 26 days. The control and KBr column were tested using the same soil column (explained in section 6.1).

Column E experiment ran for 58 days, 20 days less than column D (10x dilution leachate). This was because the concentration of leachate was much higher in E, thus requiring less time to reach the same loading capacities in column D.

Control column sampling ceased after 17 days as contaminant values showed no change. The same soil column was later used for bromide testing, because the original column set aside for bromide testing had issues with leachate short circuiting through inadequately-sealed column monolith edges. As there was no viable option for re-sealing the column without compromising the soil monolith's in-situ soil structure, the control column was the only remaining choice for use with the KBr column test in the laboratory.

The column originally intended for KBr column was never irrigated with KBr column, thus it was a worthy candidate for use in extraction of the "mini-cores" for the porosity test (section 4.4), as the soil structure was still intact and in-situ.

Select samples of collected drainage were then filtered and analysed for ammoniacal-N, electrical conductivity, total nitrogen, nitrate-N and COD in accordance with the methods specified in section 3.5. The results for these columns are shown in Appendix D, and discussed in Chapter 6.

6.1. Bromide column

Bromide column testing was conducted on Kate Valley in-situ soils to examine pollutant transport mechanisms. Bromide has proven to serve as a suitable tracer material since it is highly soluble, non-adsorptive, quantitatively measured in low concentrations and relatively inexpensive to source (Gilley, Finkner, Doran, & Kottwitz, 1990). Bromide has been used as an indicator for movement of nitrate in soils, due to similar anionic properties and high mobility (Smith & Davis, 1974). Bromide is not subjected to microbial transformations and gaseous losses, it usually has a low concentration in most natural soils, and its anion properties are repulsed by negatively charged clay particles (Clay, Zheng, Liu, Clay, & Trooien, 2004).

For the purpose of this experiment, a 2 litre stock sample of 20,000 mg/L KBr was made, as detailed in section 3.3.3. Samples were diluted to 40 mm irrigation volumes of 200 mg/L of KBr, before flood irrigation.

Analysis of bromide concentrations were conducted by Hills labs via the examination of total bromide. This was a viable analysis method for bromide (Br^-) as total bromine comprises of Br^- and Br^0; knowing concentrations of Br^0 and Br^- were negligible in soil before application, sampling for total bromine in a column irrigated with KBr will reveal the concentration of Br^- only ($KBr \rightarrow K^+ + Br^-$).

Figure 48 plots total bromine concentration analysed from pore volume samples conducted by Hills Laboratory. Total bromine levels for the first irrigation event, sampled at 65 mg/L. These levels increased steadily, almost linearly to the final reported value of 177 mg/L at almost 0.5 pore volumes (unitless).

Recalling that initial applied levels of bromide was 200 mg/L of KBr, Figure 48 shows that at 0.5 PV, the effluent PV almost samples at influent concentrations, with a difference of around 22 mg/L. Following the linear trend, estimations show that concentration of bromide in pore volumes should equal influent (peak) at around 0.55 PV (unitless) of KBr application.

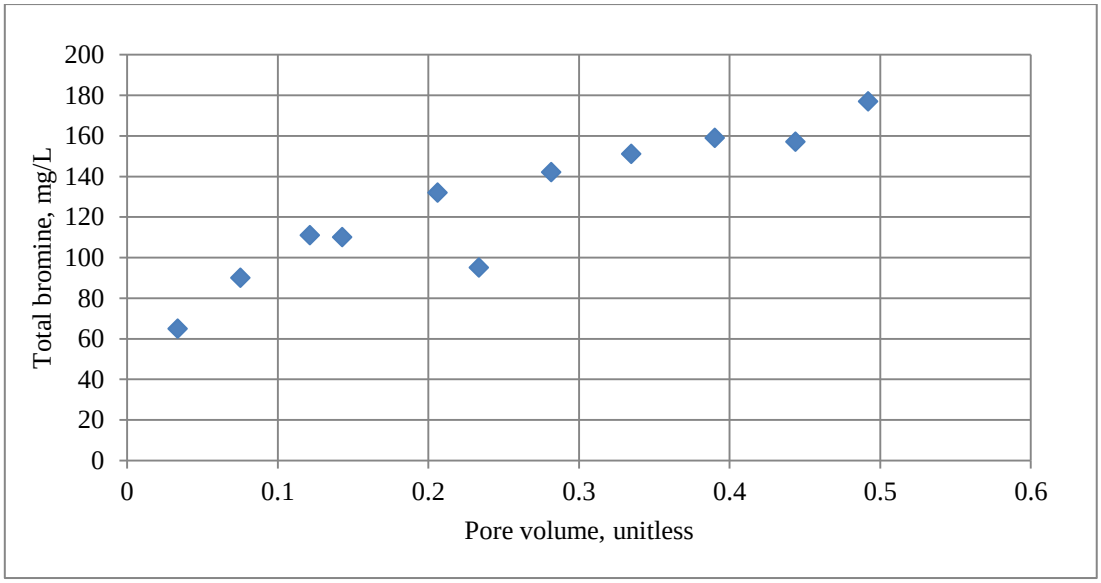

Figure 48. Total Bromine of KBr column with pore volume, unitless.

Silva, Cameron, Di, and Hendry (1999) notes that the emergence of bromide and nitrate peaks before the application of one pore volumes may indicate that not all pores had been involved in transporting solutes. If all soil in a monolith had been participating in drainage, the emergence of the peak concentrations would coincide with one pore volume of drainage. The emergence of peaks prior to the application of one pore volume may also indicate preferential flow in the soil macropores. Theory and experimental results suggest that there was soil in the column that was not participating in drainage.

Experimental observations during the irrigation period of column F were that more macropores existed than for Columns D or E. This was concluded from the majority of the KBr irrigate (average around 65% of irrigated volume) passing through the soil monolith within an hour; in comparison with columns D or E which took much longer (around 6-12 hours, longer as cumulative contaminant loading capacities increased).

Some soil erosion from the previous 8 control irrigation events occurred through existing root channels and through earthworm activity within the column. These channels were made more prominent from the delay between excavation and column use, where earthworms and plants were allowed time to cultivate (Figure 49-54); water irrigation events from the control column testing also provided a water source for plant growth. Soil erosion was evident from the loose soil particles collected from pore volume buckets and containers; although this amount (specks of soil particles) was small when compared to the relative size of each soil monolith.

Figure 49. Earthworm holes clearly present during flood irrigation of column F.

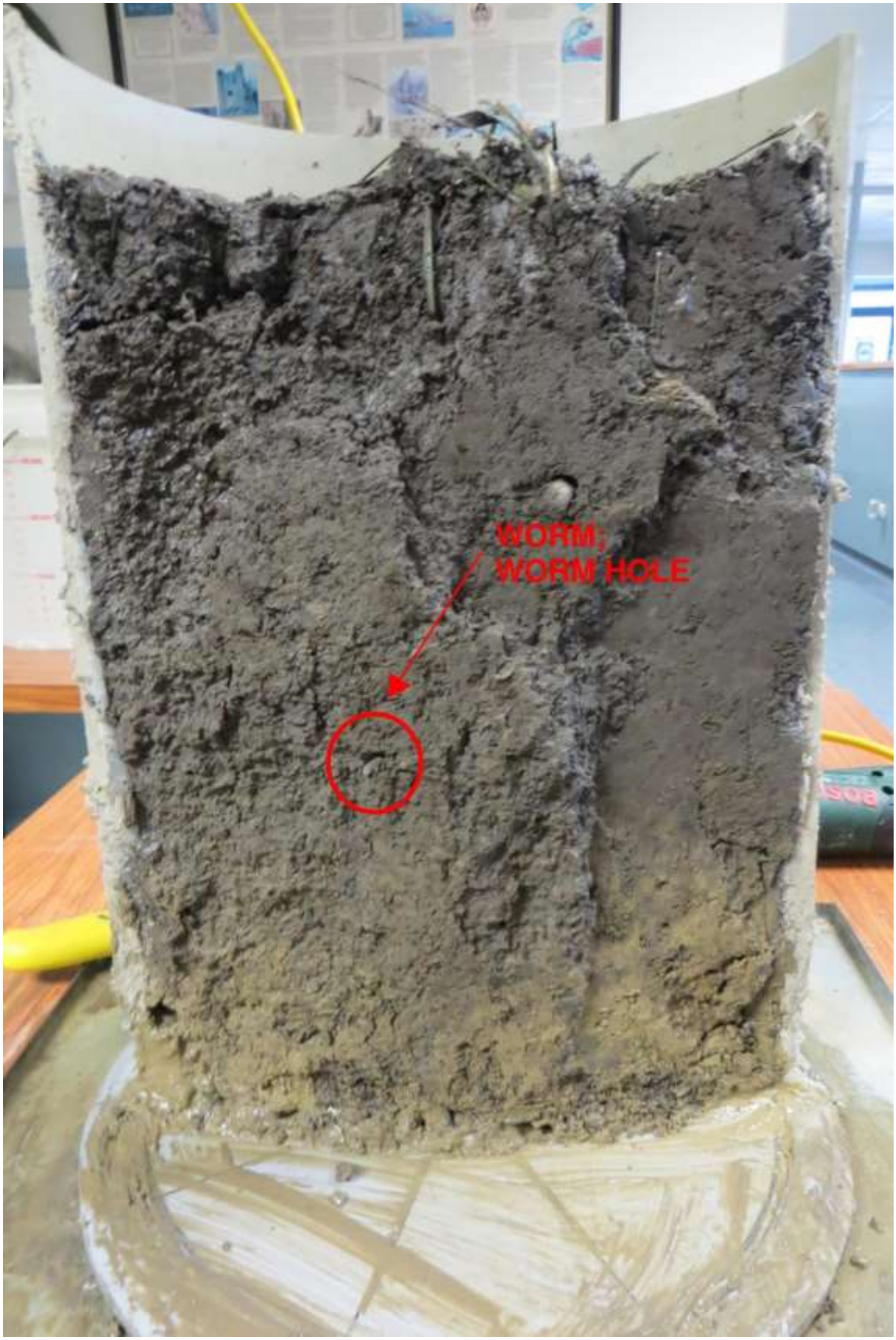

Figure 50. Column dissection of column D, showing earthworm activity.

Figure 51. Dissection of column D, vegetation layer still present in top layer.

Figure 52. Dissection of column E, evidence of root channels.

Figure 53. Cross section of column D, after experimentation.

Figure 54. Cross section of column E, after experimentation.

6.2. Column transport characteristics

Column flow rates were examined with for columns D and E. Trends generally show that the time it took for pore volumes to leach through the columns generally increased as soil became more loaded by contaminants. The decrease in flow rate varied with the dilution of the leachate.

Figure 55 plots the flow rate permeating through column D throughout the 78 day experimentation period. Flow rates were calculated from dividing collected pore volumes (ml) by the time it took to collect them (hr). Figure 55 shows that column flow rate were originally quite rapid at an initial 200 ml/hr, these flow rates steadily decreased as more dilute leachates were applied, eventually levelling off at around 50 ml/hr after 2 PV (unitless) (~ Day 70), towards the end of the experiment. Flow rate was steady around 50 ml/hr between 1-2 PV (Day 30-70), this could indicate loading capacity of the soil, as no further soil particle surfaces are available for adsorption thus influent contaminants are less likely to adsorb so they continue travelling down and out of the column (the increase of pore volume contaminant concentrations).

A similar behaviour is seen in Figure 56 which plots flow rate of column E, 2x leachate dilution over the 58 days of sampling. Figure 56 shows an initial average drainage rate of around 50 ml/hr, less than the initial 200 ml/hr of D (Figure 55), though it took more PV (unitless) in column E's case for stabilisation of flow rate at 20 ml/hr (unitless; around 1.2-1.4 PVs) (Around day 33-48) of application.

Initial slow drainage rates of column E are likely a combination of highly concentrated leachates (2x dilution leachate) occupying adsorption sites at a faster rate than that of column D, which uses a relatively more dilute leachate irrigate (10x dilution leachate).

It is also worthy to note that not all in-situ soils have the exact same transport properties. Granted these differences should be small, given proper site selection and extraction methods, but soil structure and history will vary.

Zhong (2012) investigated bioclogging effects in columns with his study, where hydraulic conductivity decreased sharply to 18.32% of the original value on the 12^{th} day of sampling, by the end of the experiment, a reduction of more than 1 order of magnitude was observed.

Based on variations in hydraulic and biochemical parameters, Zhong (2012) has grouped the process of bioclogging into 4 stages:

1) Severe clogging, aerobic microorganisms reproduce rapidly in the inlet (top soil layer).
2) Clogging spreads through entire column and hydrodynamic dispersion increases sharply as microorganisms (aerobic and anaerobic) reproduce.
3) Anaerobic microorganisms reproduce rapidly and produce more gas, hydrodynamics decrease quickly.
4) Aerobic and microorganisms multiply continuously and hydrodynamic dispersion, hydraulic conductivity and porosity decrease steadily, until a steady stage is reached.

Variables between this study and Zhong (2012)'s include different column dimensions, soils, irrigate, irrigate volume, microbial community, and irrigation methods. These all inherently contribute towards differences in results for comparison; however, some fundamental observations can be used to explain occurrences in this study.

Viewing column D (Figure 55) as an example, hydraulic conductivity can be seen to rapidly decrease (almost linearly) between 0-0.5 PV (unitless) (Day 1-18). Beyond 0.5 PV (unitless) (Around day 18), step 4 of Zhong's process of bioclogging can be observed, where hydraulic conductivity reaches a steady state (50 mm/hr).

Zhong (2012)'s Step 3 process of anaerobic microorganisms reproducing rapidly to produce gas is an example which wouldn't compare to this study, as these leachate columns were speculated to be highly aerobic (air was free to permeate column between irrigation events). Zhong (2012)'s column study was conducted with continuous flow. This introduced oxygen between irrigation events may have substituted for anaerobic microorganism's gas production, decreasing hydrodynamics through the soil column.

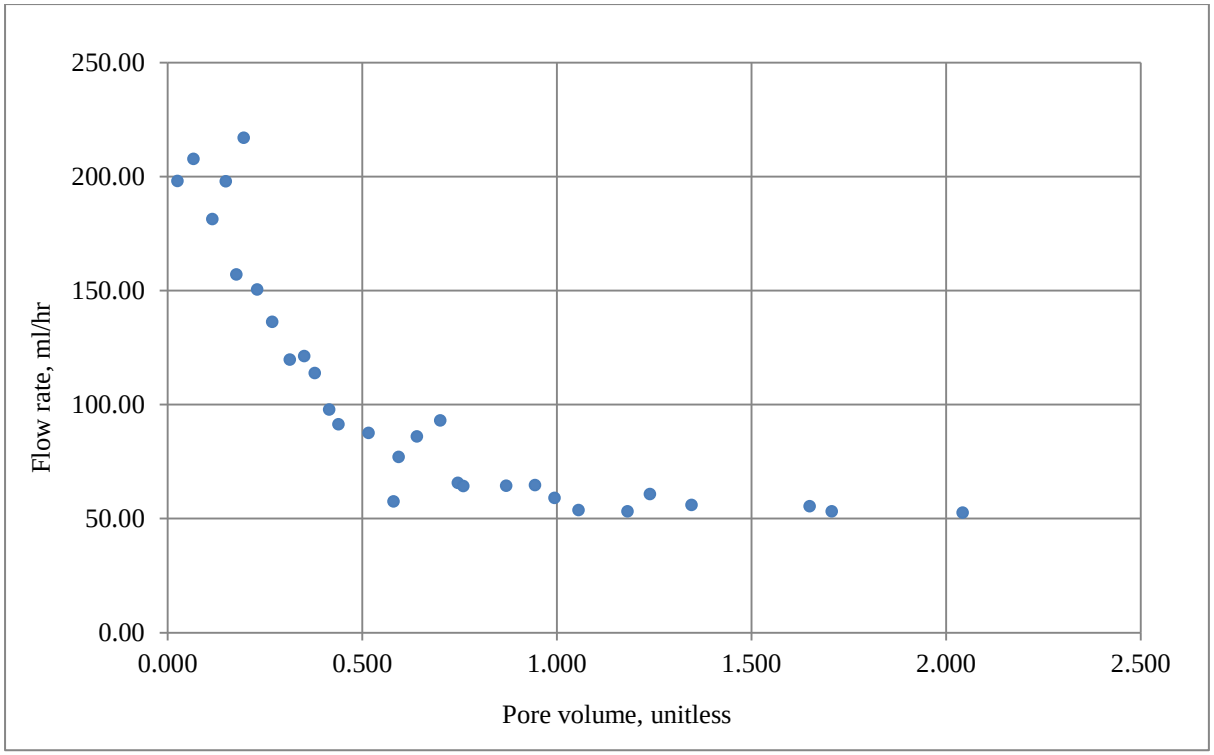

Figure 55. Leachate flow rate through soil monolith D with pore volumes, unitless.

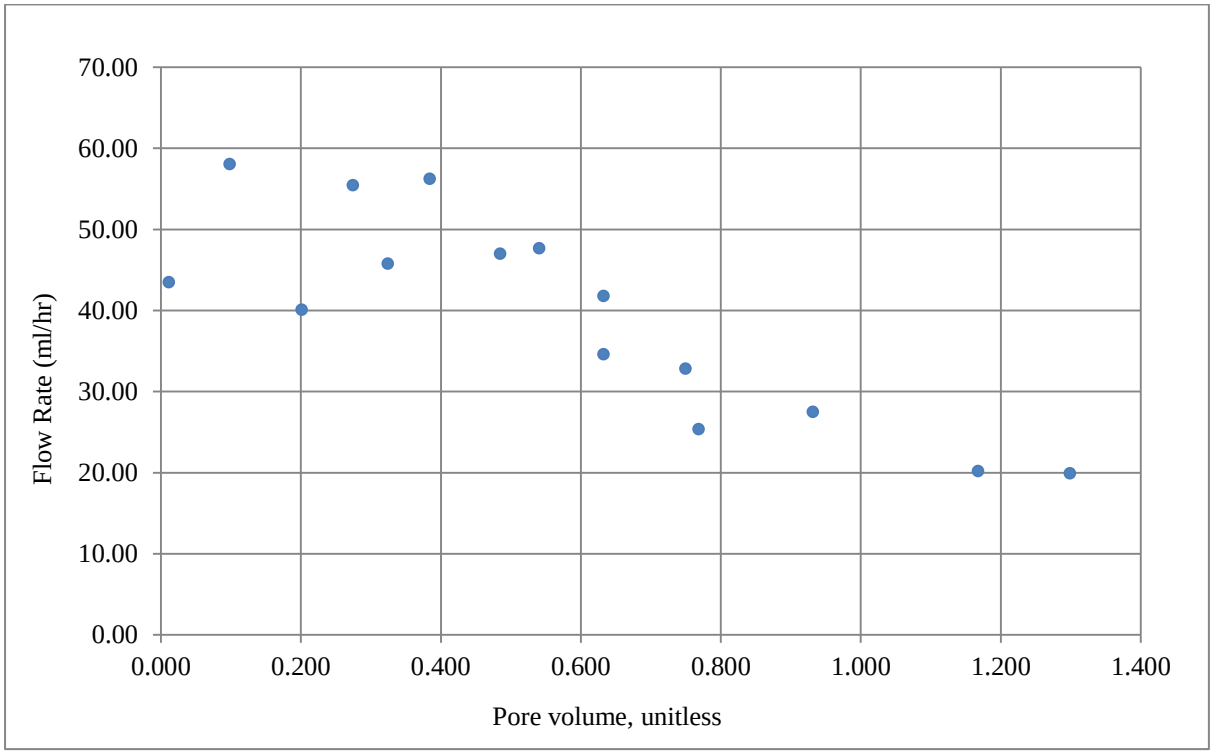

Figure 56. Leachate flow rate through soil monolith E with pore volume, unitless.

6.3. pH

pH was examined in control column F over 16 days of experimentation. Knowing the pH of de-ionized water was sampled at 6.37 (Appendix D.4), the drainage from column F ranged between 8.04 to 8.28, averaged 8.16 with a standard deviation of 0.08. This range comprised of initial sampled PV pH of 8.04, gradually increasing to pH 8.2.

Figure 57 plots column D's range of PV pH results. There appears to be significant scatter between pH values within the reported range of 6.83 to 8.06, averaging 7.64 with a standard deviation of 0.2942. The lower reported average drainage pH will be due to interactions between dilute leachate and soil within the soil monolith.

The reported equilibrium average pH of 7.64 in drainage is reasonably neutral. There appears to be no increasing or decreasing trend for pH in the 10x dilution leachate case, as reported values are subjected to large scatter.

Figure 58 reports the drainage pH of column E (2x dilution leachate) over 58 days. pH values also remained relatively consistent, with a reported range of pH 6.22 to 8.88, averaging 7.62 with a standard deviation of 0.5163.

As pH values did not change drastically in soil monoliths (like that of batch test experiments), in-depth analysis of these results is unnecessary. The reaction of soil monoliths with the application of high strength leachates were not as reactive as batch cases, likely due to the tested soils not being oversaturated with dilute leachate (30 g of soil with 70 ml of dilution leachate).

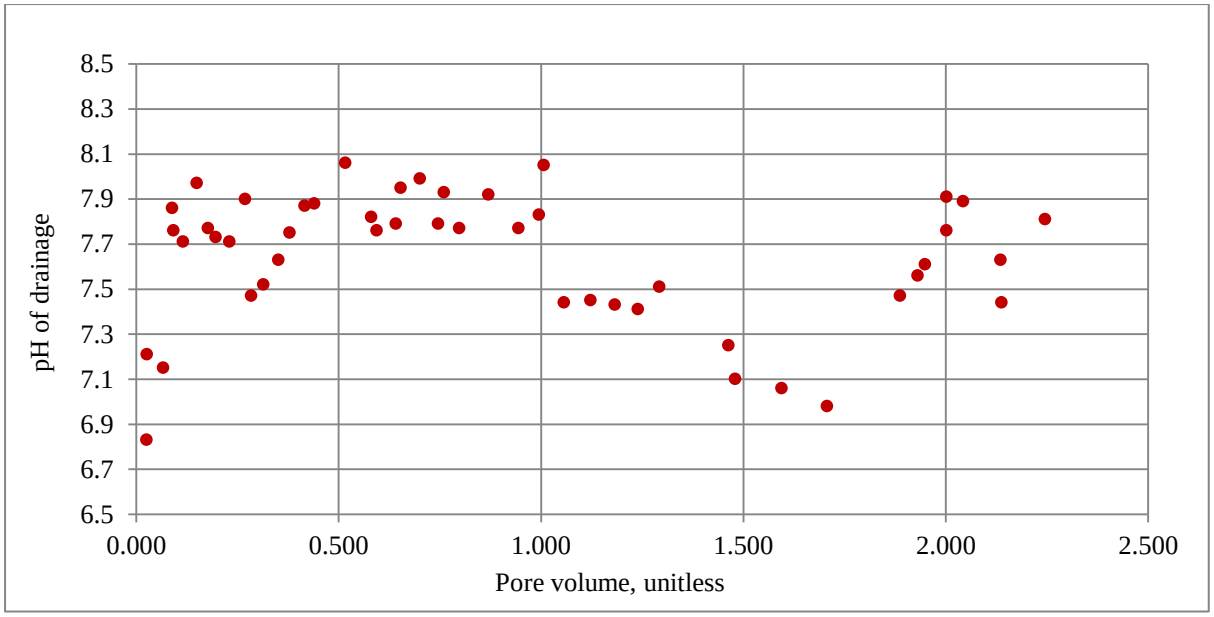

Figure 57. pH of 10x raw leachate dilution column D with pore volumes, unitless.

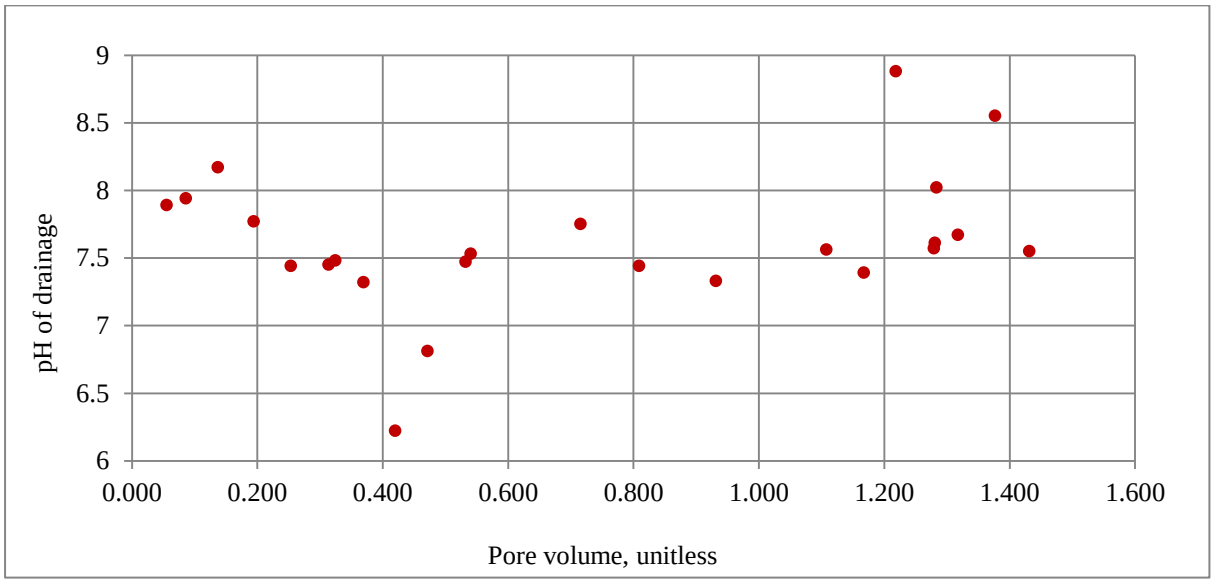

Figure 58. pH of 2x raw leachate dilution column E with pore volume, unitless.

6.4. Electrical conductivity

Control behaviour of electrical conductivity in soils were initially tested in column F. Knowing that de-ionized water initially sampled at 1.9 µS/cm, the range of conductivity values obtained through the 16 day experimentation period ranged from 404 – 442.7 µS/cm.

Figure 59 plots the concentration of electrical conductivity flushed from the 10x dilution leachate column D. The results show that column D soil was initially efficient at removing conductivity from diluted leachate, decreasing initial conductivity values from 1136 µS/cm to around 500 µS/cm. From here, conductivity linearly increased in the sampled drainage water to around 800 µS/cm before reaching what appears to be a breakthrough at 0.49 PV, and then stabilising above influent concentrations around 1700 µS/cm.

It is interesting to note that initial drainage EC values in column D sampled closely to drainage from the control column; where column D sampled around 50 µS/cm above the control case.

To address the stabilized effluent EC being higher than initially sampled 1136 µS/cm of 10x dilution leachate; it may be a result of a low reading when collecting initial EC data for dilution leachate, or some other electrostatic mechanism and/or interaction within the monolith between soil and leachate, releasing EC from column into pore volumes.

Figure 60 plots electrical conductivity data for drainage from column E. Initial conductivity in 2x dilution leachate sampled at 8140 µS/cm, over the 58 day experimental period, soil in column E showed similar behaviour as that of column D, where soil was initially relatively efficient at removing conductivity (sampling effluent PV at 1000 µS/cm) and after subsequent loading, a breakthrough was observed around 0.2 PV (unitless). Sampled conductivity values never reached influent concentrations of 8140 µS/cm, drainage conductivity may never reach influent concentrations, this can only be examined with further column drainage analysis past the 58 days.

Experimental accuracy of conductivity was generally very agreeable between dilution ratios. The highest discrepancy through all soils using the same dilution ratio was the 2x raw leachate dilution of 476 µS/cm. It should be noted that conductivity values of more concentrated leachates such as raw and 2x dilution took significant amounts of time for values to stabilize with probe in solution. All readings were subsequently taken 10 seconds after full probe submersion in solutions.

Given the need for drainage to be filtered through 0.45 micron filters before sampling, not a lot of leachate was available for submersion (filters tend to degrade after 10-15 ml of drainage pass through; filters were a limited resource). To counteract this, filtered drainage were measured from a thin measuring cylinder, which was just wide enough to fit the conductivity probe. Full submersion of the entire conductivity probe was achieved in all cases from 20 ml samples of dilution leachate.

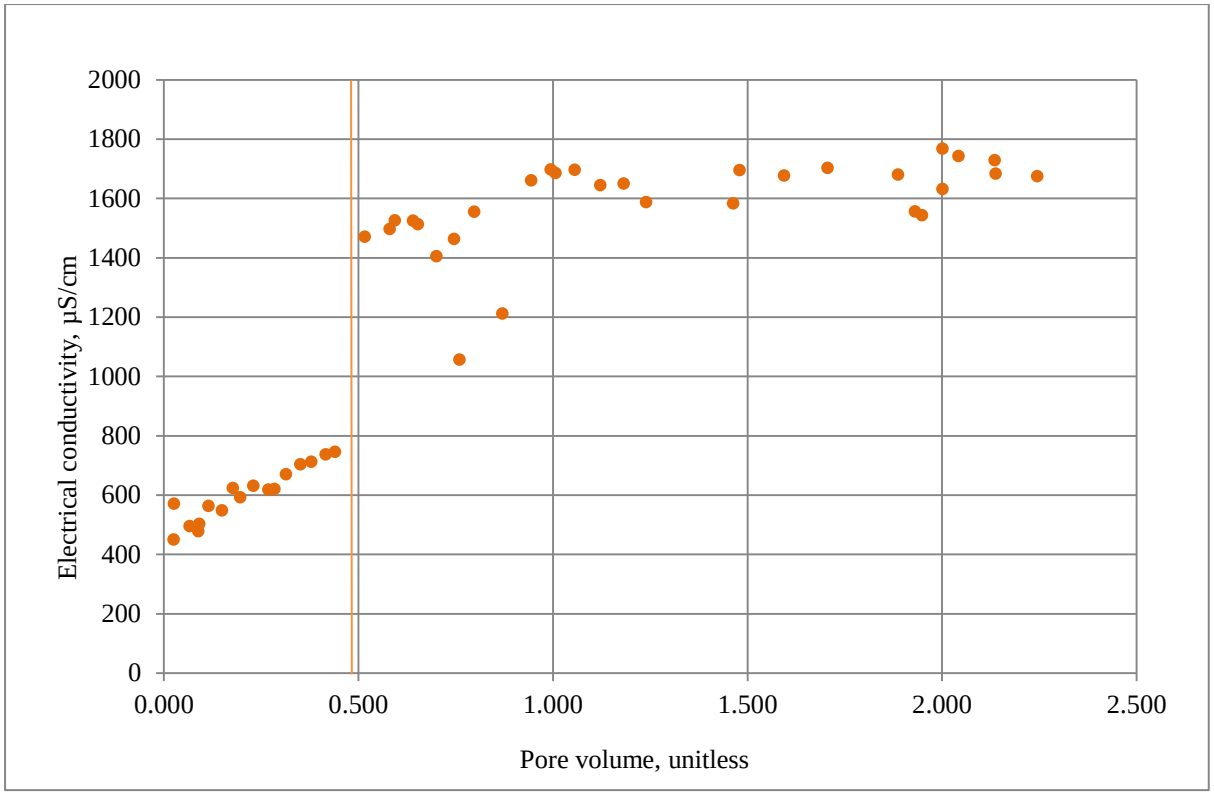

Figure 59. Electrical conductivity of 10x raw leachate dilution column D with pore volumes, unitless.

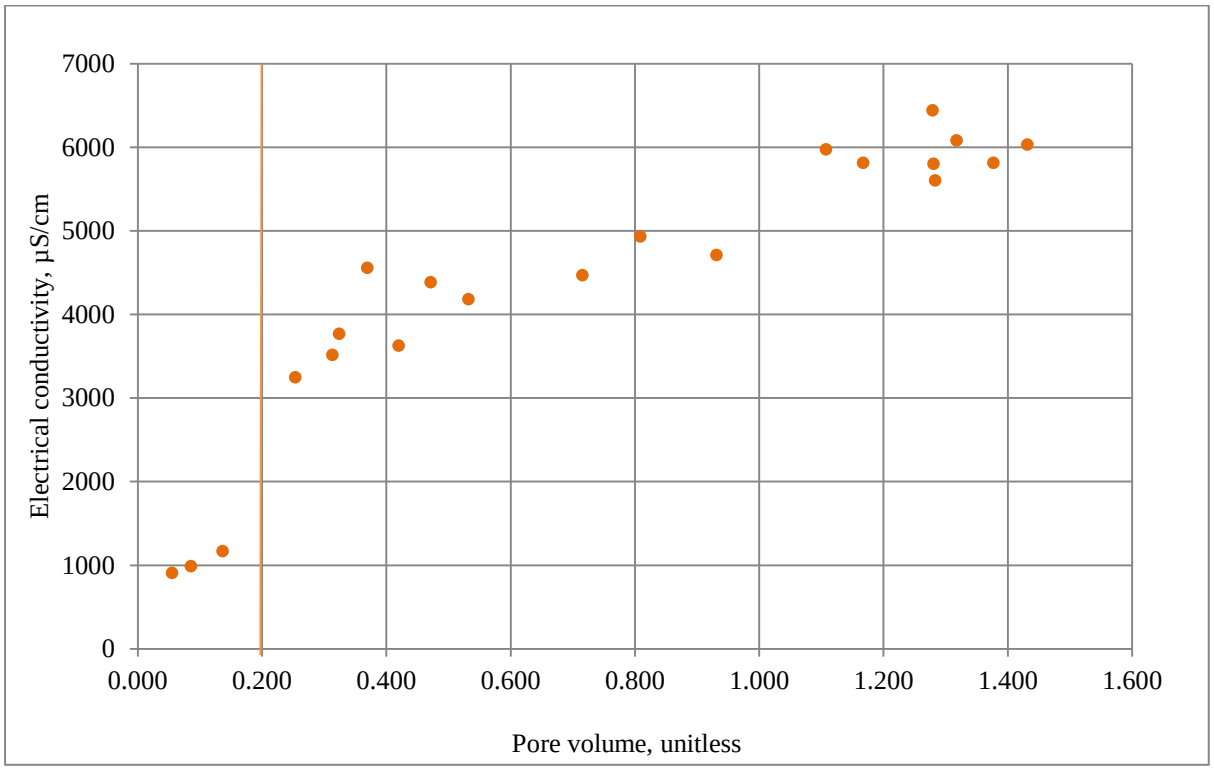

Figure 60. Electrical conductivity of 2x raw leachate dilution column "E" with time, hr.

6.5. Chemical oxygen demand (COD)

COD behaviour was initially examined in column F through a 16 day trial using de-ionized water as irrigation. Knowing that the initial COD level of de-ionized water was initially 0 mg/L, any increases in COD of pore volumes would have likely been washed from the soil column. From observing the sampled data, COD values from column F revealed no trends, as sampled COD values ranged from 4-45 mg/L.

Figure 61 plots reported COD values of column D over 78 days. The 10x diluted leachate applied to this column had a COD of 307 mg/L. Drainage from the column seemed to average around 100 mg/L from 0-1 PV, results averaged slightly higher around 150 mg/L of COD between 1-2.25 PV. A few outlier results were sampled up to 521 mg/L; these reported concentrations were likely due to experimental errors.

It appears that these bi-daily applications were insufficient in loading (concentration) to overcome the capacity of the soil. Other possible reasons may be the microbial activity in the column, breaking down part of the relatively dilute COD concentrations. The soil's capacity to recover through microbial activity was not examined in depth as it was not within the scope of this study.

Figure 62 plots reported COD values of column E over the irrigation period of 58 days. Knowing the influent COD was 1535 mg/L for 2x dilution leachate, treatment of COD through soil column E was initially highly efficient, bringing down the COD concentration to around 20-30 mg/L. Values steadily increased to around 400mg/L at 0.4 PV, where large scatter was observed between the range of 400-1000 mg/L; afterwards, sampled COD values seemed to increase from 1.1-1.5 PV following in the linear pattern previously established from 0-0.4 PV range.

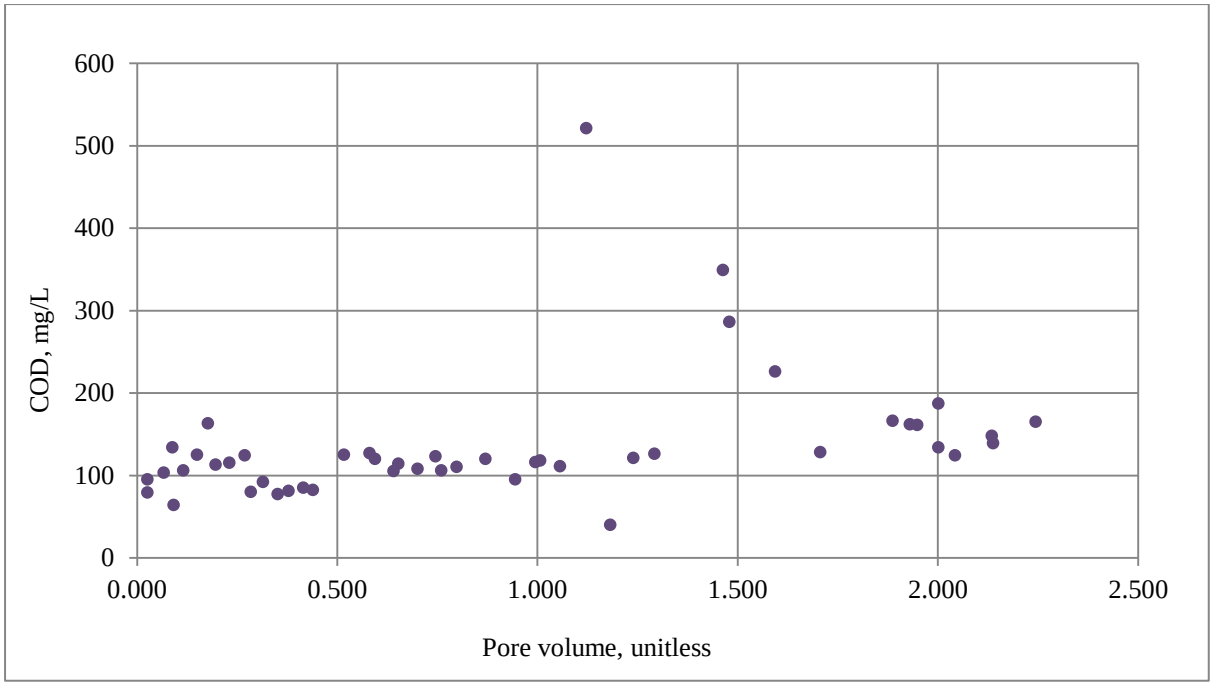

Figure 61. COD of 10x raw leachate dilution column "D" with pore volume, unitless.

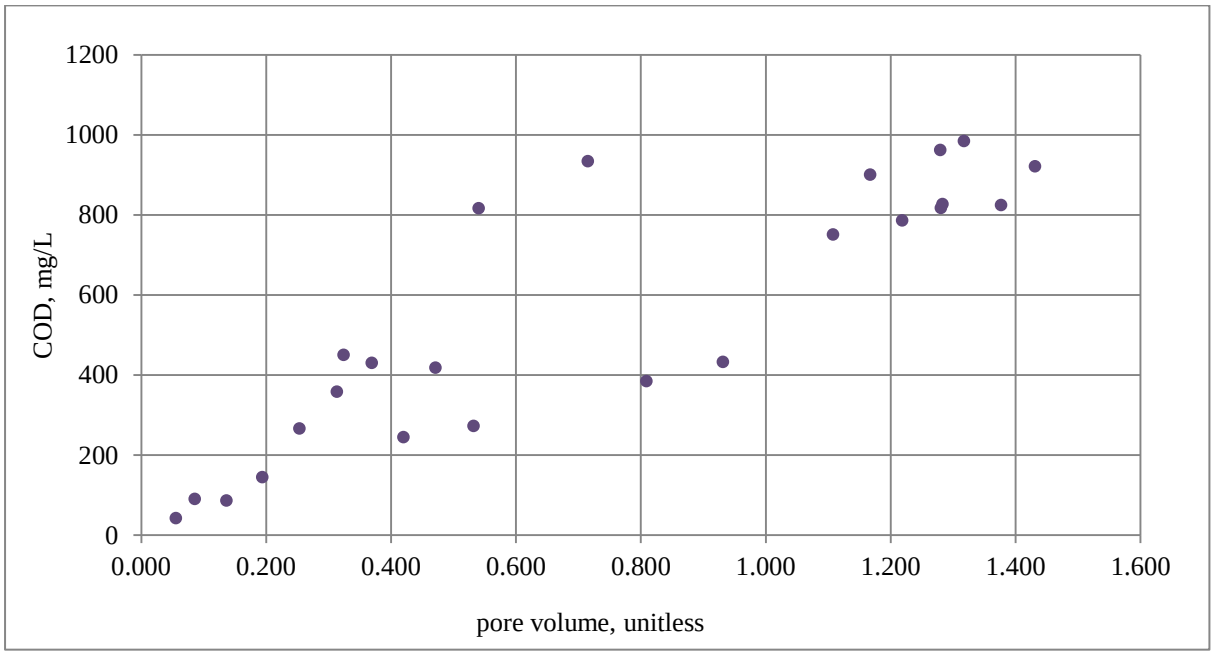

Figure 62. COD of 2x raw leachate dilution column "E" with pore volumes, unitless.

6.6. Nitrogen

To gauge accuracy of the nitrogen results, a split sample of drainage samples were sent to an external commercial analysis by Hills Laboratory. A comparison between the two results should give an indication on the accuracy of sampled concentrations by the student.

The selected samples were drainage from columns D and E, collected on 17 September 2013. The results are shown below in Table 15.

Table 15. Comparison of results and Hill's laboratory samples.

	E54.1 (17 Sep)	E, Hills Results	% Difference from value	D34.1(17 Sep)	D, Hills Results	% Difference from value
Total Nitrogen, mg/L	90	79	13.92	61	58	5.17
Ammoniacal-N, mg/L	65.6	59	11.19	<0.4	12.4	-
Nitrite-N, mg/L	-	0.02		-	2.7	
Nitrate-N, mg/L	1.6	0.02	7900.00	37.2	42	11.43
TKN, mg/L	-	79		-	13.4	
Total Organic Nitrogen, mg/L	-	20		-	<1.1	

% difference was calculated by taking the difference between student and Hill's sampled values and dividing by the Hill's values, multiplied by 100 (convert to percentage).

The results sampled by the student were generally higher than that detected by Hills Lab, with the exception of nitrate levels in column D, where a -11.43% difference was observed between results.

Results are within agreement to within 15% difference, which is sufficient accuracy for the scope of this study as important trends in reported values will likely still be distinguishable.

6.6.1. Ammonia

Ammonia concentrations in soil columns were initially investigated with control column F over 16 days. The reported values of ammoniacal-N ranged between 0.0-0.1 mg/L of ammoniacal-N. This was as expected, as there was no ammoniacal-N concentration in de-ionized water, nor in that of the collected in-situ Kate Valley soil monoliths (Table 4).

Figure 63 plots drainage ammoniacal-N concentration for column D, irrigated with 10x diluted leachate with an influent concentration of 111 mg/L of ammoniacal-N. Ammoniacal-N concentrations are all relatively low in column D, between 0-15 mg/L over the irrigated 2.25 PV (unitless) range; note that reported values were roughly ± 2 mg/L over this range. For ammonia concentrations, trends were not easily discernible for column D, thus total nitrogen data will be used to interpret sorption results (section 6.6.3)

The -13 mg/L drop around 1 PV (unitless) might be explained by a brief break in irrigation of column D. The column was left for around 3 days to examine the ability of the soil to recover from leachate application; it could be that this allowed for an equilibrium to be established which then allowed more ammonia attenuation. It would seem the biological and chemical mechanisms in the soil were able to treat/sorb the ammonia of column D's dilute leachate. The extended break between irrigation could have also allowed oxygen to re-enter the soil column, allowing for various chemical and or microbial processes facilitating nitrification, leading to conversion of ammonia into subsequent nitrogen species such as nitrates. Another possible explanation for the "inconsistencies" in reported values may include oxygen interference during experimentation, sampling and storage of drainage water.

Ammoniacal-N levels in 2x leachate dilution column E sampled between the range of 0-250 mg/L, as shown by Figure 64. A gradual increasing trend could be observed from 0-1.2 PV (unitless), then as sampled concentrations became larger (around 250mg/L), values began subjected to large scatter, sampling at 40 mg/L, then back to 240 mg/L, then back down to around 40 mg/L (towards the end of column E's sampling period).

Discrepancies in reported ammonia values could include the aforementioned oxygen related issues inherent during experimentation, sampling and storage of pore volume samples.

Data for ammoniacal-N was chosen to calculate the partitioning coefficient for 2x dilution leachate used in column E. The blue line in Figure 64 represents the estimated breakthrough in contaminant, at 1.25 PV.

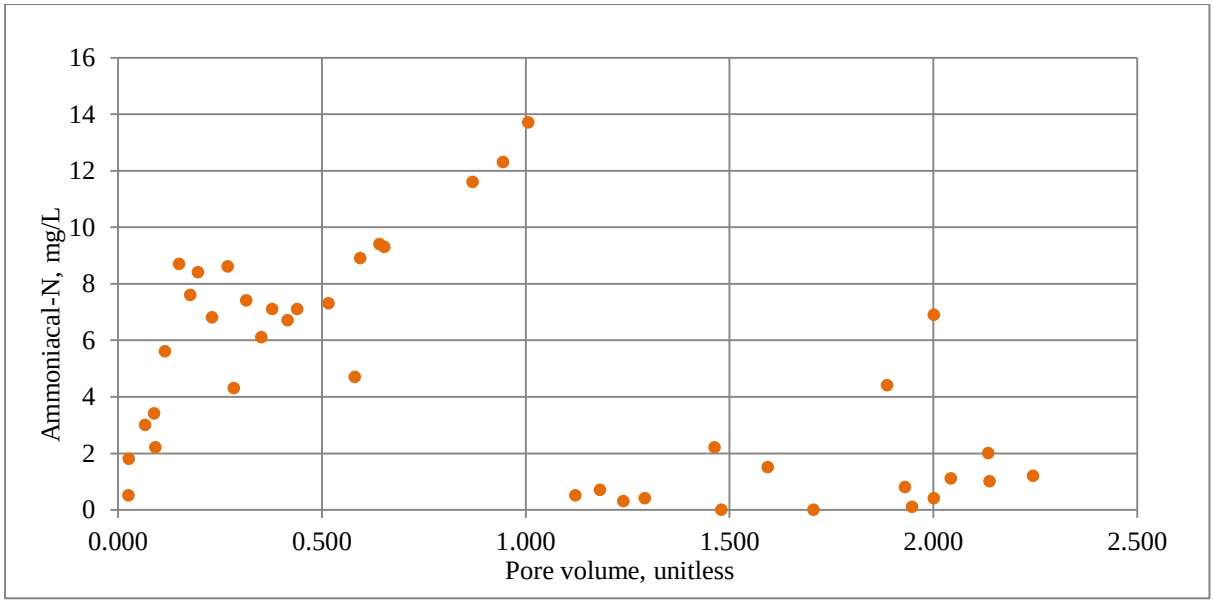

Figure 63. Ammoniacal-N of 10x raw leachate dilution column "D" with pore volume, unitless.

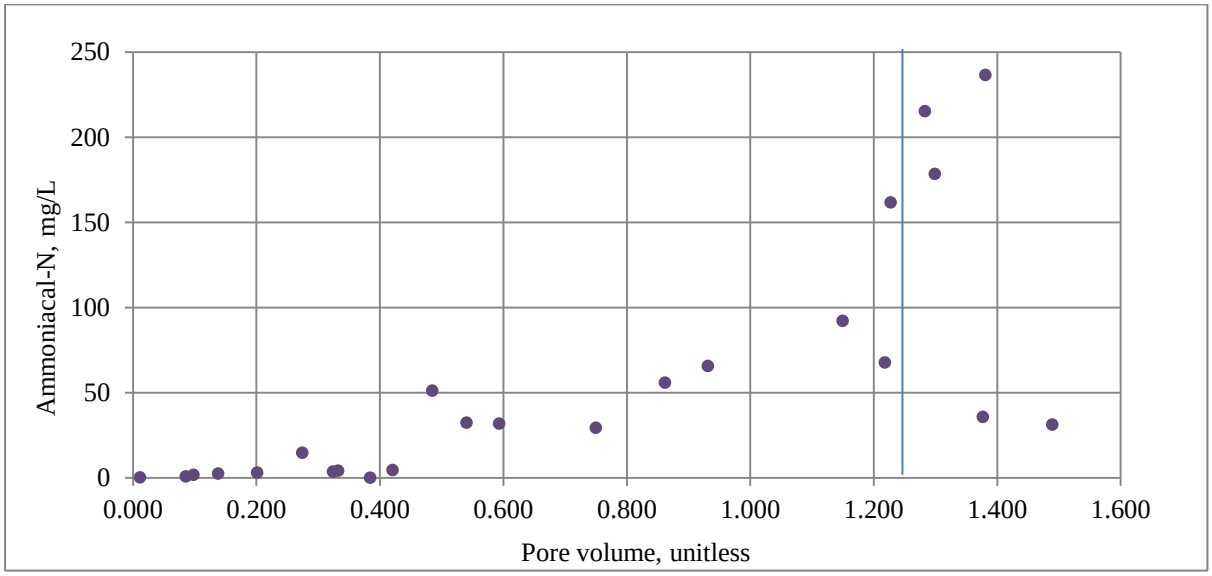

Figure 64. Ammoniacal-N of 2x raw leachate dilution column "E" with pore volume, unitless.

6.6.2. Nitrate

Nitrate-N concentrations were analysed with column F as a control case. 40 mm of de-ionized water was irrigated every second day for a total of 16 days. Reported nitrate-N concentrations in the control column ranged from 2 - 9.5 mg/L of nitrate-N, and showed no apparent trends. The increases in nitrate-N concentrations tested in drainage would have been washed from the soil, as initial applied de-ionized water contained 0 mg/L of nitrate-N. It is not uncommon to detect concentrations of nitrate-N from first drainage, as nitrate-N exists in natural soils as part of the nitrogen cycle, providing nutrient source for plants.

Drainage nitrate-N concentration from column D is shown in in Figure 65. Column D was irrigated with 10x dilution leachate, with an initial nitrate-N concentration of 0.6 mg/L.

Nitrate-N results for column D increase from an average of around 10mg/L of nitrate-N to its peak sampled values of around 60mg/L at 1.5 PV (unitless). From 1.5 PV, a decline was observed down to an average of 35 mg/L around 2.25 PV (unitless).

Scatter is inherent throughout these values also, likely a combination of the introduction of oxygen during experimentation and sampling affecting the sampled values, comparison of sampled data with Hill's Laboratory showed discrepancies to be within the range of ±10 mg/L of nitrate-N.

Increases in nitrate-N concentration are the result of nitrification of ammoniacal-N while diluted leachate travelled through the columns. The effectiveness and degree of nitrification is dependent on various soil properties such as drainage, existing loading, and more so on types and amount of microbial activity.

Possible explanations for the decline in nitrate levels from 1.5 PV (unitless) onwards could include the adaptive nature of microbes in soil, where microbial adaptation has facilitated more efficient ways of assimilating ammonia-N concentrations in soil strata, thus resulting in less ammonia to be nitrified to nitrate-N.

Sampled nitrate-N for column E's 2x dilution leachate is shown in Figure 66. Column E averaged below 5 mg/L from 0-1 PV (unitless) of application, these values rose sharply after 1 PV to around 22-68 mg/L, given there were not many sampled points to support the increase in nitrate-N concentration beyond 1 PV (unitless). Reasons for these large increases and decreases of nitrate-N levels may include the previously mentioned issue with introduced oxygen during experimentation and sampling of the dilution leachate and drainage.

On average, sampled nitrate-N levels were below that of 10x dilution leachate in column D; although both increased to around the same peak concentrations, only after 1 PV (unitless) of application, around 60-70 mg/L. Possible explanations for a lower concentration average of nitrate-N in stronger dilution leachate may be due to the high influent ammoniacal-N concentrations, impeding the soil's microbial ability to nitrify it into nitrate-N, thus leaving more effluent ammoniacal-N in pore volumes; resulting in lower nitrate-N (as it was never converted from ammoniacal-N).

This theory is supported by the examination of ammoniacal-N data from 6.6.1, where from examining the range of 0.4-1 PV (unitless), 2x dilution leachate (Figure 64), ammoniacal-N concentration averaged around 50 mg/L; in comparison to Figure 63 where ammoniacal-N never exceeded 14 mg/L below 1 PV (unitless).

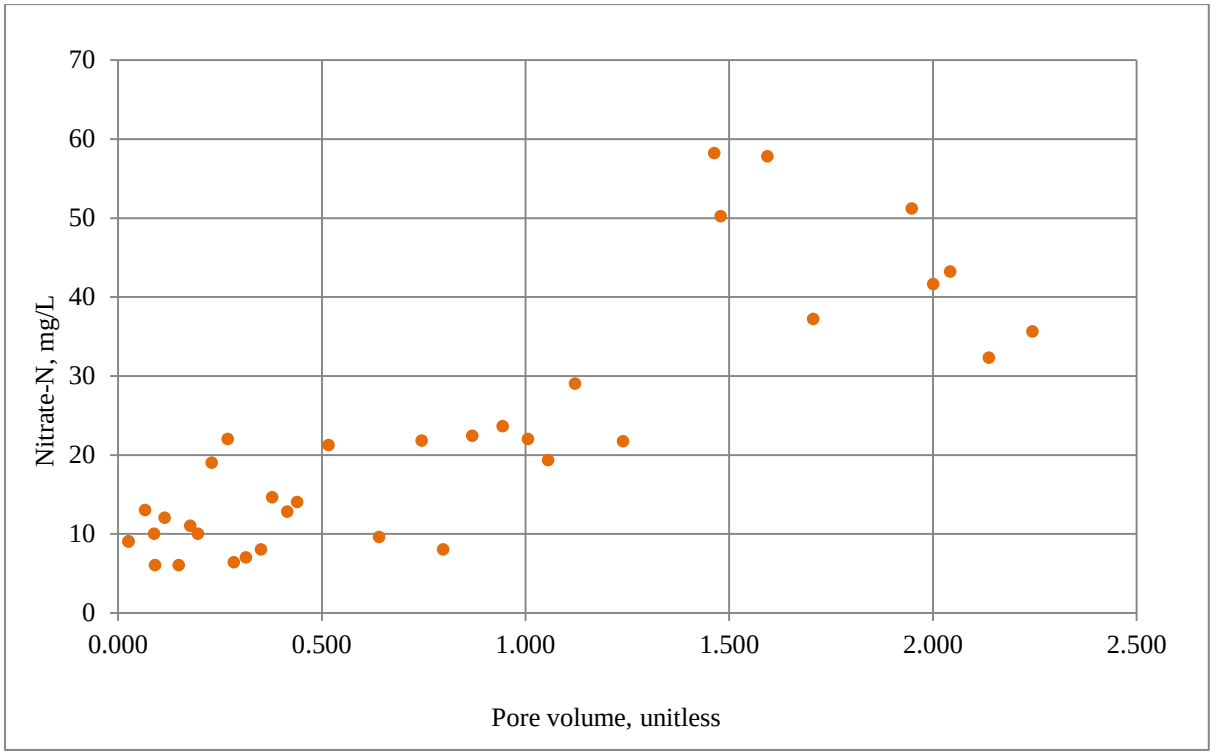

Figure 65. Nitrate-N of 10x raw leachate dilution column D with pore volume, unitless.

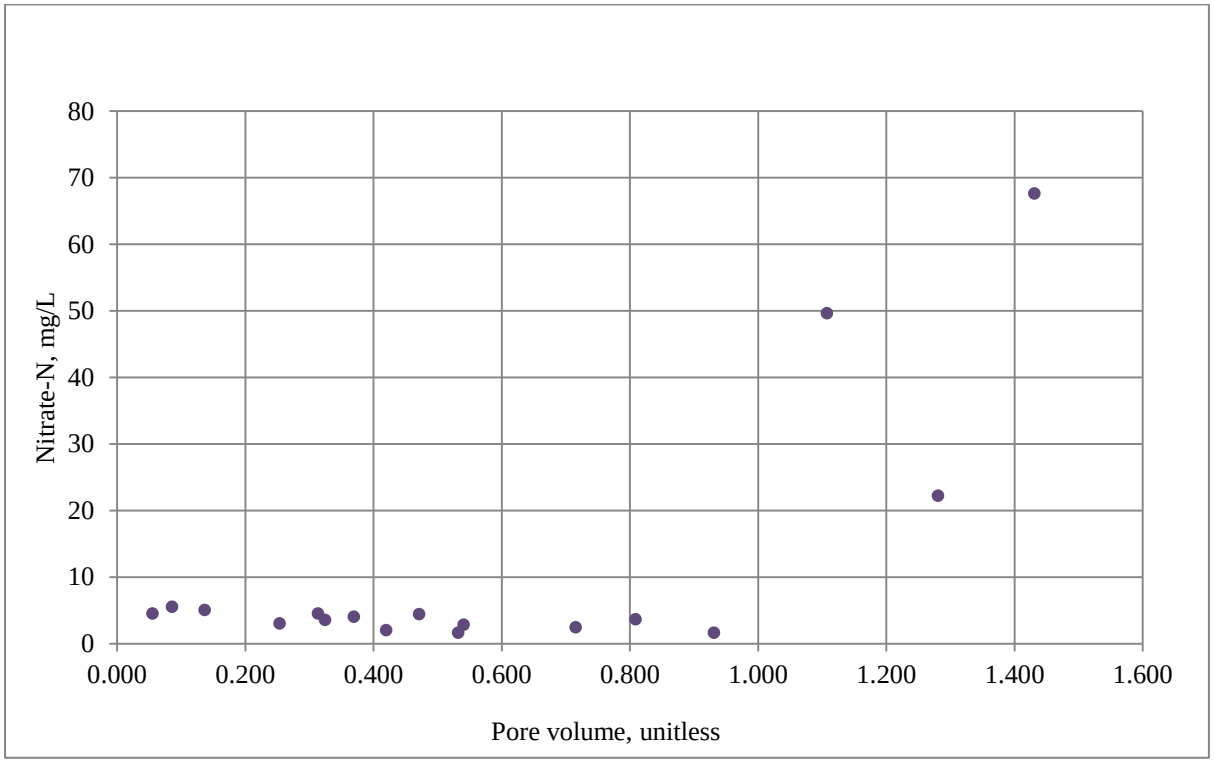

Figure 66. Nitrate-N of 2x raw leachate dilution column E with pore volume, unitless.

6.6.3. Total nitrogen

Total nitrogen sampling of control column F's pore volumes was inconclusive. Over the 16 day sampling period, 3 samples were selected for total nitrogen sampling, these pore volumes were collected on day 1, 7, and 13. All three tested sampled under the detection limit of the total nitrogen test of 10 mg/L. This was not surprising as initial concentrations of total nitrogen in de-ionized water was 0mg/L, and mobile, soluble total nitrogen concentrations in Kate valley soil would have been low.

Total nitrogen was only sampled every 3-4 pore volume collection events, this was to address the relatively time-consuming lab analysis procedure and the limited resources available to conduct these.

Figure 67 plots the total nitrogen concentration of column D, irrigated with 10x dilution leachate. Initial irrigate sampled total nitrogen at 135 mg/L influent concentration. The first pore volumes sampled around 10mg/L, this steadily increased to 60 mg/L around 1.2 PV (unitless) where a slight increase in sampled concentrations can be observed. The peak of total nitrogen concentrations have not been reached for column D, even after the extensive 78 days of sampling, reasons for this is like due to the relatively dilute nature of leachate used for column D, in combination with the soil's microbial capacity for conversion of nitrogen species.

Total nitrogen removal was calculated at an initial 125mg/L of removed, this linearly decreased to around 35 mg/L of removal around 2 PV (unitless) of application. The combination of sampling period and dilute leachate nature was likely a favourable combination and allowed sufficient recovery time for microbial and chemical activity in soil strata of column D to process the nitrogen concentrations.

Figure 68 plots total nitrogen concentrations in drainage from column E, irrigated with 2x raw dilution leachate. Initial total nitrogen concentration for 2x leachate dilution was tested at 675 mg/L.

The detection limit was near 10 mg/L for total nitrogen with this method, and so high uncertainty existed in the range of 5-10 mg/L. As a result, it is hard to draw conclusions about the differences between the columns at these low concentrations. From 0.4 to 1 PV, total nitrogen concentrations climbed steadily to around 95 mg/L.

Above 1 PV, total nitrogen in column E “peaked” rapidly to just above 200 mg/L, then concentrations are observed to decrease. This is interesting as similar behaviour can be observed in column D also around 1.2 PV, where a similar peak of 90mg/L was observed. Concentration of column E then drop off to around 65 mg/L at 1.7 PV (unitless), before increasing again to around 100 mg/L after 1.9 PV. Data points above 1.4 PV (unitless) were not obtained in the experiment. Likely possible explanation for this is the previously mentioned conversion of nitrogen through various processes (section 6.6.1.), and the extended break between leachate irrigation.

Total nitrogen removal can be compared between columns D and E by examining their drainage total nitrogen concentrations at identical PV (unitless). Taking 0.5 PV, column D exhibited 115 mg/L removal, from an influent 135 mg/L concentration to a 20 mg/L pore volume concentration. Soil in column E removed 615 mg/L of total nitrogen, from an influent concentration of 675 mg/L, to a final pore volume concentration of 60 mg/L. At 0.5 PV (unitless), removal percentages equate to 85% and 91% for columns D and E, respectively.

Using high strength leachates for irrigation will initially induce high total nitrogen content removal, however, the ability of the soil to keep nitrogen removal high quickly degrades, as shown from the drop in total nitrogen removal from 91% to 14.8%, from 0.5 to 1.0 PV (unitless) respectively, in column E. Column D initially removed 85% of total nitrogen from leachate, 6% less than E at 0.5 PV, however, at 1.2 PV, nitrogen removal was still considerable a decrease of 64%.

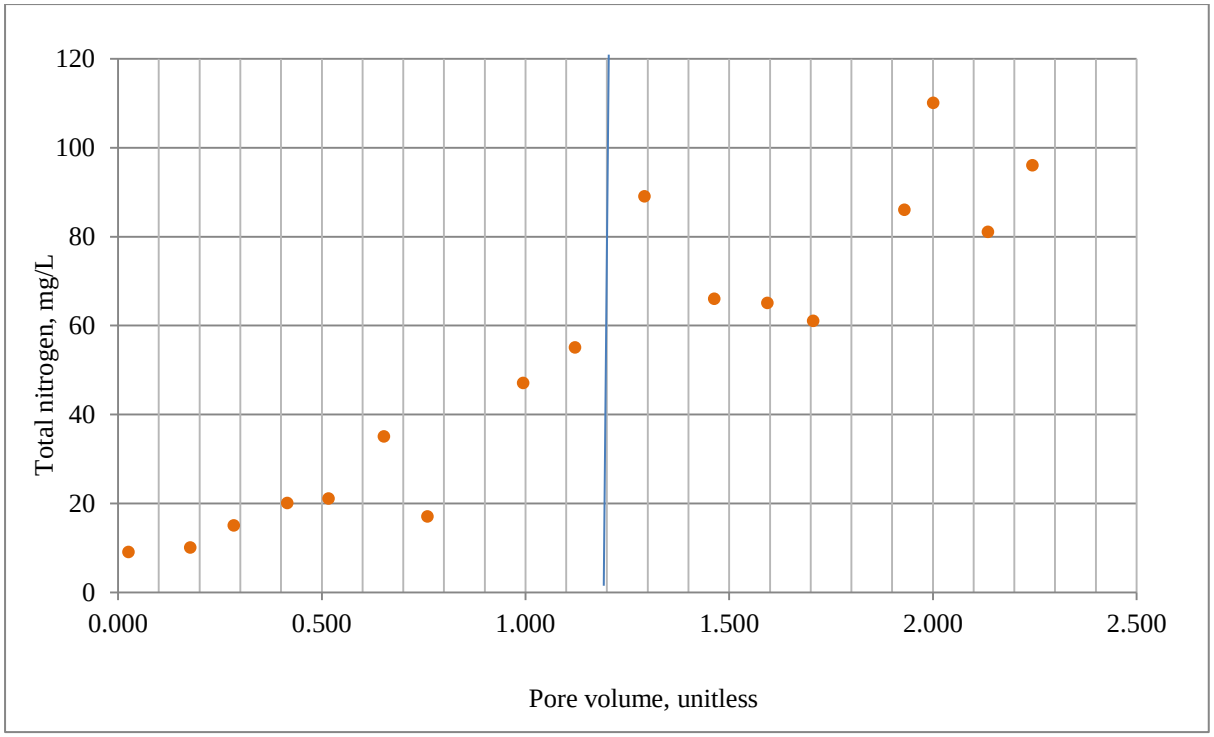

Figure 67. Total-N of 10x raw leachate dilution column D with pore volume, unitless.

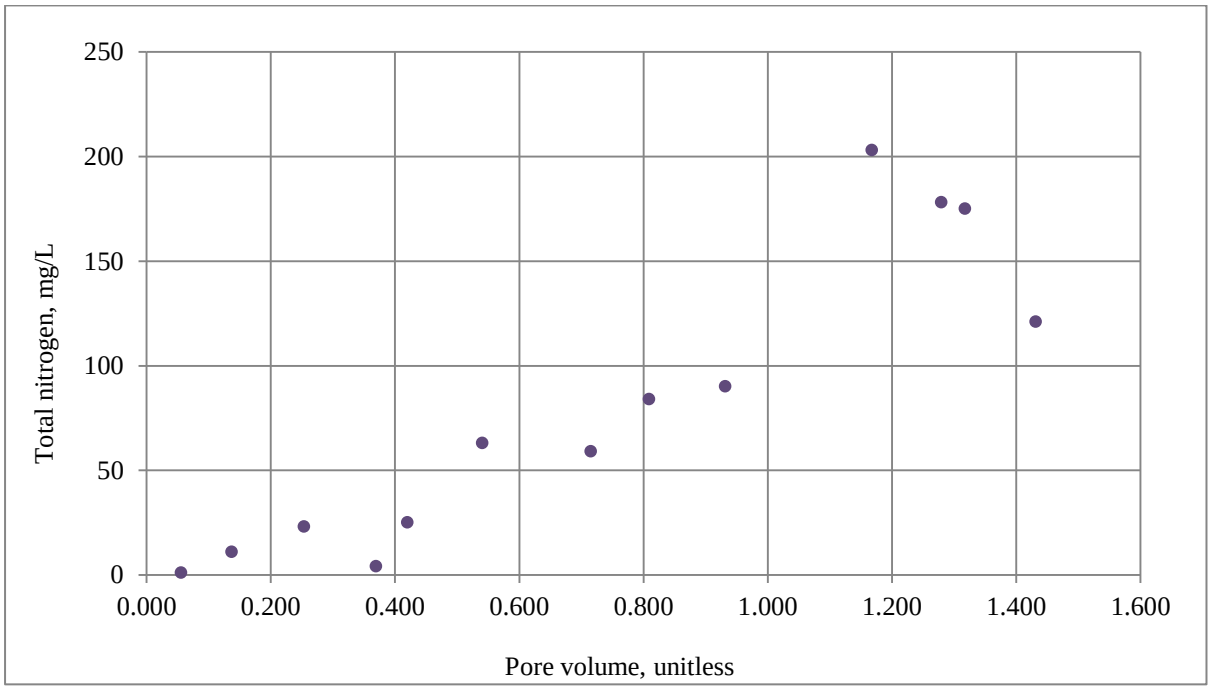

Figure 68. Total-N of 2x raw leachate dilution column "E" with pore volume, unitless.

6.7. Post column experiment discussion

Post experiment soil samples from columns D and E were sent to Hills Laboratory for analysis. As shown by Table 16, all layers were tested for pH, K, Mg, Na, CEC, organic matter, total carbon, total nitrogen, olsen-P, and total carbon. Also included in Table 16 is original soil concentration before experimentation. This allows for a direct comparison on the impact that leachate irrigation has had on soil chemistry.

Table 16. Post column experiment soil concentration results from Hills Lab.

	Initial soil concentrations			**Final soil concentrations**					
	0-20	20-40	40-60	E0-20	E20-40	E40-60	D0-20	D20-40	D40-60
pH	8	8.3	8.3	8.7	8.5	8.4	7.6	7.8	8.1
Olsen-P, mg/L	7	8	9	10	8	6	7	6	7
K, me/100g	0.12	0.13	0.12	0.86	0.79	0.59	0.18	0.11	0.16
Ca, me/100g	8.7	12.1	11.7	5.5	7.0	5.2	7.6	7.7	10.7
Mg, me/100g	1.09	1.56	1.42	0.88	0.64	0.57	0.79	0.82	1.05
Na, me/100g	0.07	0.16	0.2	1.4	1.41	1.34	0.37	0.36	0.42
CEC, me/100g	10	14	13	9	10	8	9	9	12
Organic Matter, %	0.5	0.6	0.5	0.7	0.4	0.6	0.5	0.4	0.4
Total Carbon, %	0.3	0.3	0.3	0.4	0.2	0.4	0.3	0.2	0.2
Total Nitrogen, %	<0.04	0.04	<0.04	0.07	0.07	0.06	0.05	<0.04	<0.04

Prior to any experimentation, pH was sampled by Hills lab to be 8 at the topsoil level, and increasing by pH 0.3 to 8.3 for 20-60 cm soil depths. When initial results are compared to column E (2x dilution leachate irrigation), pH can be seen to increase by 0.7 to 8.7 for topsoil, +0.2 to 8.5 for 20-40 cm soil, and +0.1 to 8.4 for 40-60 cm soil. Trends observed include larger pH differences in soils closest to the surface topsoil. This is also apparent in column D, however, pH is seen to decrease by -0.4, to 7.6 for topsoil; -0.5 to 7.8 in 20-40 cm soil, and -0.2 pH to 8.1 in 40-60 cm soil. The similar trend observed between columns D and E is that pH deviates from initial concentrations the most in uppermost layers, closest to topsoil. Reasons for this may be that (1) finer particles in deeper soils have a stronger buffering capacity to resist pH changes, or that (2) most reactions occur in the upper layer of the soil column as they are the irrigate's first contact.

The lower sampled final soil pH values in column D may be due to the dilute nature and more neutral pH of leachate irrigate in Column D (previously discussed in section 5.1).

Cation exchange capacity of the soils are seen to decrease from an initial measured range of 10-14 mg/100g to 8-10 mg/100g in column E, and 9-12 mg/100g in column D.

Total nitrogen was expressed as a weight % in tested soils; initially less than the detection limit of 0.04 %. This is relatively negligible and it is coherent with what was observed in the control column experiment. We expect low nitrogen in the soils because the patch of land where soil was extracted had no previous agricultural activity, and was not within the vicinity of any runoff paths. Nitrogen levels retained in soils for column D almost remained below detection limit, with the exception of topsoil sampling at 0.05% total nitrogen. The highest increase in total nitrogen was observed in column E soils, where % of total nitrogen was 0.7% in 0-40 cm soil layers and 0.6% in 40-60 cm soil layer. This source of total nitrogen will most likely consist of ammoniacal-N and nitrate-N, irrigated from the strong 2x dilution leachate; and from various biological processes (e.g., nitrification) in soil.

7. Final Discussion

7.1. Further column discussion and study

Ammoniacal-N data was used to examine sorption behaviour for column E. Knowing the value of the retardation factor, the partitioning coefficient for ammoniacal-N in column E can be calculated as $5*10^{-8}$ L/mg, using Equation 7 with 35% porosity and a soil density of 1780 kg/m^3 for Greenwood formation soil (Transwaste Canterbury, 2002). Total nitrogen was used to estimate partitioning for column D, as issues persisted with ammoniacal-N sampling where scatter was large and values were sampled low, averaging below 14 mg/L. This was likely a combination of nitrification, oxygen related interferences and microbial activity.

From Figure 67, the blue vertical line denotes the region where breakthrough was interpreted to be for total nitrogen. this would yield a partitioning coefficient of $4*10^{-8}$ L/mg for total nitrogen in column D using porosity of 35% and soil density for greenwood formation of 1780 kg/m^3 (Transwaste Canterbury, 2002).

Higher sorption potential in column E may be due to the more concentration nature of 2x dilution leachate irrigate used. This effectively increases the amount of contaminants flooding the column, providing more contact opportunities of contaminant sorption onto available soil particle surfaces.

Although the results suggest that partitioning of contaminants occurred at a higher capacity in column E (2x leachate), this doesn't necessarily mean that column E is the better solution. Soil was visibly more polluted in column E along with a slight "rubbish" odour. Vegetation on topsoil layer had all been "poisoned" to death. This was in contrast with column D, where soil still seemed viable and vegetation were still alive (slight yellowing on weeds).

Table 17. Batch and column Kd and R factor comparisons (porosity = 35%, density = 1780 kg/m^3).

Experiment	K_d (L/mg)	Retardation Factor
Batch 0-20 cm soil	$9.5*10^{-7}$	5.83
Batch 20-40 cm soil	$7.2*10^{-7}$	4.66
Batch 40-60 cm soil	$6.4*10^{-7}$	4.25
Column D	$4*10^{-8}$	1.20
Column E	$5*10^{-8}$	1.25

Table 17 summarises calculated K_d and R values between the batch and column tests. Immediate observations include the discrepancies between values calculated from batch and

column experiment; where batch test's R factors ranged 4.25-5.83 and column test only ranged 1.20-1.25.

Weiner (2007) notes that for dissolved neutral organic molecules (such as nitrogen), their sorption to soil is controlled mostly by organic portions of the soil, explaining why sorption was observed higher in soil layers closer to the surface, where organic matter was highest (1% more volatile solids in topsoil when compared to soil from 60 cm depth [see volatile solids test, section 4.3.]); also Table 16 Hills laboratory data, where organic matter % was highest in topsoil layers, ranging from 0.7 to 0.4 % and 0.6 to 0.4 % (through all soil depths) for columns E and D respectively. Also from Table 16, total carbon was highest in final soil concentrations ranging from 0.4-0.2 % for column E, and 0.3-0.2 % for column D.

This gap between observed K_d values may be due to several reasons:

The concentration of leachates used between column and batch tests did not correlate exactly. Batch tests were conducted over the range of raw-50x leachate dilution; column tests used 10x and 2x leachate dilution as irrigate. The range of batch tests conducted technically covered the values used in column tests, however, a more accurate comparison could be drawn had batch tests been conducted using 2x and 10x leachate dilution.

Batch tests were designed to maximize sorption potential between soil particles and leachate. Batch mixing facilitated exposure of soil particle surfaces to leachate contaminants for sorption reactions, and also thinning of the soil particle boundary layer from this liquid exposure. In contrast with the column test, not all soil in the column reached their sorption potential, reasons for this may include preferential flow within the column, relatively low exposure time between leachate and soils, and formation of barriers either from in-situ soil structure or biological means. Calculations made in batch and column tests (for sorption potential) assumed full participation between soil particle surfaces and leachate contaminant constituents. This assumption was more accurate in batch than column tests.

Further contributing to the discrepancies between batch and column results is the method in which K_d and R were determined. Batch tests used Equation 8 to calculate R from an interpreted K_d, using plots from batch results; column tests interpreted an R value from BTC and calculated K_d from Equation 8. Whether or not batch and column K_d and R values can ever be tested to agreement remains inconclusive (within the scope of this experiment), however, results obtained from column tests should be favoured when considering the

application of leachate irrigation, because they are more similar in nature to the real world application than that of the batch tests.

The optimal goal in these experiments would be to find the strongest applicable leachate concentration that causes negligible detrimental impacts on the soil structure, microbiology and flora population in the long-term and short-term. When only examining the soil and dilute leachate interactions, laboratory experiments of batch and column test observations suggest it will be necessary to dilute raw landfill leachate by around 10 times (or more) for sufficient negligible detrimental impacts on the soil structure and resident flora.

The above recommendation was derived from the examination of 2x (column F) and 10x (column D) dilution leachate column experiments. In other countries, the use of irrigation management strategies such as rotation area irrigation, seasonal irrigation, silvi-culture management, irrigation method, have proven to noticeably decrease the amount of dilution required for raw leachate before sustainable application. Leachate irrigation to land should still be assessed on a case-by-case basis due to unique leachate contaminants and environments in which they are released.

Further studies that could complement the leachate sorption potential of Kate Valley soils would be to extend column tests for longer periods of time, and to observe the long-term interactions between soil and leachate. Sampling drainage from columns at more frequent and steady intervals may provide more visible trends in plotted BTC data.

It could be beneficial to examine and quantify the effect that aerobic column conditions have on nitrification within the column, as some of the sparse data has been speculated to be the result of oxic conditions.

It would also be interesting to examine the plant, soil, leachate interactions. A study could consider how flora could be used to remove nitrogen from leachates as nutrients to enhance growth and increase nitrogen removal.

Lastly, examining the functions of the soil's microbial community and their interactions with the soil-leachate dynamic would help explain much of the behaviour observed in plotted BTC and batch data. Quantifying these populations and understanding their favourable conditions may also reveal methods or best management practices in which to enhance nitrification, thus decreasing nitrogen concentrations in drainage.

8. Conclusions

Landfill leachates have been found to vary in contaminant constituents and concentration, determined by the intake waste, method of storage, and age of landfill. These varying aspects govern the mechanisms and methods of landfill leachate disposal, thus thorough characterisation of landfill leachate is the first, if not most important step towards safe discharge onto land.

Current practices in landfill leachate irrigation to surround lands have been studied by the likes of N. W. Macdonald, Rediske, Scull, and Wierzbicki (2008); and Smesrud, Duvendack, Obereiner, Jordahl, and Madison (2012), where success in irrigation practices have been mostly attributed to structural best management practices, after thorough leachate contaminant characterisation, and consideration of local discharge to land guidelines.Comprehensive guidelines for discharge to land in the NZ context includes SCION's Biosolids guidelines and NZWWA (2003)'s "Best management practices for applying biosolids to forest plantations in New Zealand"; which classifies use of biosolids to land under 3 categories. Kate Valley leachate was classified under this guideline as "type Ab, restricted use", where limiting constituents were salinity and nitrogen content.

Soil sieving was conducted on collected Kate Valley soil. Soil from the 0-20 cm depth consisted mostly of coarse sand at 62%, medium sand of 35% and the rest consisted of fine sands/silts and lost fractions. 20-40 cm soil layer had slightly less coarse sand (58%), and more medium sand (39%) than 0-20 cm topsoil. The deepest soil layer sampled (40-60 cm) had the least coarse sand of 48%, highest medium sand at 46%. The amount of coarse sand decreased and medium sands tend to increase as soil depth increases.

Volatile solids tests conducted showed that the average of % volatile solids in each respective soil layer decreased by about 1% from 4.32% to 3.33%, for 0-20 cm to 40-60 cm soil respectively. Higher organic content in the shallow soil layer may facilitate higher chemical soil-leachate interactions.

Porosity tests conducted averaged 35%, 36% and 43% for 0-10 cm, 10-25 cm and 25-40 cm soil depths respectively. The geological region in which soil samples were extracted from would suggest correlation with Transwaste Canterbury (2002)'s reported Greenwood formation porosity of 30%.

Batch tests were conducted through varying combinations of soil depth and dilution leachates used. Soil depths tested consisted of 0-20 cm, 20-40 cm and 40-60 cm; while tested liquid leachates included: control case, raw leachate, 5x, 10x, 20x, 35x, and 50x raw leachate dilution. Batch solid to liquid ratios were conducted with 30g of soil with 70 ml of soil, with an agitation period of 24 hours. 4 hours were allocated immediately after agitation to allow for sample settling, before centrifugal separation and subsequent filtering of liquid samples for analysis. Parameters tested in batch results consisted of pH, COD, electrical conductivity, total nitrogen, ammoniacal-N, and nitrate-N.

Large scatter in reported results was observed in COD experiments. The results showed that the type of soil had more of an impact on COD adsorbance per soil mass basis than varying leachate dilution used. This was likely attributed to higher organic matter content of shallower soil layers. On average 40-60 cm soil released less mg of COD/mg of soil (~ 0.0002 mg COD/mg soil) than 20-40 cm (~ 0.0025 mg COD/mg soil), and 20-40 cm soil releasing less mg of COD than 0-20 cm (~ 0.0030 mg COD/mg soil).

Batch ammoniacal-N concentrations for the control case sampled low across all soil layers, ranging from 0.3-1.05 mg of ammoniacal-N/L in equilibrium batch liquid. These concentrations were existent in the soil, as ammoniacal-N would sample 0 mg/L in de-ionized water. Partitioning coefficients were determined from ammonia results in all soils, and decreased as soil depth increased from $9.5x*10^{-7}$ to $6.4*10^{-7}$ L/mg for 0-20 cm soil to 40-60 cm soil respectively; suggesting deeper soils are less effective at sorption of ammonia than shallower tested soil layers.

4 in-situ soil monoliths were extracted from the forested slope region of Kate Valley landfill's site. Actual extracted in-situ soil monoliths measured 230 mm in diameter by 1500 mm in height.

Each column was used to test different irrigating conditions, although one column was found to have a leak through its sealed sides, leaving 3 soil columns to experiment with. The tested conditions for each column were 2x dilution leachate, 10x dilution leachate, and the last column was first tested as a control column and subsequently tested as the bromide column.

Irrigating conditions were scheduled roughly every 48 hours, the irrigating volume was experimentally set at 40 mm, which, given the column's circular exposed surface of 230 mm,

resulted in a 1520 ml application. Drainage was collected at least once after subsequently after irrigation loadings.

Total testing times for column for 2x dilution column was 58 days, 10x dilution was tested for 78 days, control for 17 days, and bromide column for 26 days.

For the bromide column test, influent concentrations contained 200 mg/L of KBr. From the sampled total bromine results, drainage would attain influent concentrations at around 0.55 PV (unitless). Results from this test should be considered with caution as the soil column was riddled with worm holes, a result of extended period of time between column excavation and the experiment.

Column D flow rates were initially relatively fast (200ml/hr). This steadily decreased as dilute leachates were applied; at around 2 PV (unitless) (Day 70), flow rates slowed down to 50 ml/hr. The same trend was observed for higher irrigate application of column E (2x dilution leachate), where initial drainage rates of 50 ml/hr slowed to 20ml/hr around 1.2-1.4 PV (unitless) (Day 33-48). The retardation of hydraulic conductivity through both columns are likely explained by Zhong (2012)'s explanation for bioclogging, a result of a combination of aerobic/anaerobic microorganism reproduction from the introduced dilution leachate. The effect of bioclogging varied by strength of dilution leachate applied, where more concentrated leachates experienced higher bioclogging, resulting in lower hydraulic conductivity.

COD in column D had an influent concentration of 307 mg/L. This was reduced to 100 mg/L between 0-1 PV. Drainage COD concentrations rose to around 150 mg/L by 1-2.25 PV, with a few outliers sampling up to 521 mg/L, a result likely of oxygen interference in testing. Original influent COD concentrations in column E sampled at 1535 mg/L, where initial drainage sampled around 20-30 mg/L (first few drainage samples); this steadily increased to 400 mg/L at 0.4 PV where large scatter was observed when sampling drainage above 400 mg/L; also attributed to oxygen interference through experiment and sampling stages of COD measurement. Soil's interaction with microbiological processes and their effects on COD have a noticeable effect on COD results sampled. Processes involved with microorganisms were outside the scope of this study.

Ammoniacal-N concentration for the 10x dilution leachate column ranged between 0-15 mg/L over the 78 day irrigation period, down from an initial influent concentration of 111

mg/L. Breakthrough points were not easily discernible from the plotted figure, thus BTC analysis was conducted using column D total nitrogen data. Reasons for the scatter in results have been attributed to oxygen interference during experiment and sampling periods of the column, along with a break in irrigation to analyse this effect on drainage concentrations. 2x dilution leachate column ranged between 0-250 mg/L of ammoniacal-N. Gradual increasing trends were observed between 0-1.2PV (unitless), subsequent reported values were subjected to scatter.

Nitrate-N concentrations in 10x dilution leachate irrigation column initially averaged around 10 mg/L, up from an initial 0.6 mg/L concentration in influent irrigate. This steadily increased to around 60 mg/L at 1.5 PV (unitless), which then declined to an average of 35 mg/L around 2.25 PV (unitless). Increases in nitrate-N concentrations are the result of nitrification, dependent on soil, microorganism activity, and available ammoniacal-N concentration in solution for conversion. Nitrate-N concentrations in 2x dilution leachate averaged around 5 mg/L between 0-1 PV (unitless). These values rose to around 22-68 mg/L at 1 PV (unitless). Possible explanations for a lower concentration average of nitrate-N in stronger dilution leachate may be due to the high influent ammoniacal-N concentrations, impeding the soil's microbial ability to nitrify it into nitrate-N, thus leaving more effluent ammoniacal-N in pore volumes; resulting in lower nitrate-N (as it was never converted from ammoniacal-N).

Total nitrogen concentration in 10x dilution leachate column initially sampled around 10 mg/L, down from an influent concentration of 135 mg/L. Drainage concentration increased to 60mg/L around 1.2 PV (unitless). The entire breakthrough curve of column D was not observed with sampled total nitrogen results, even after 78 days of sampling. This may have been due to the dilute nature of leachate used. More time may have resulted in observation of breakthrough. The 2x raw dilution leachate column sampled total nitrogen around 96 mg/L from 0.4-1 PV (unitless); above 1 PV (unitless), concentrations rapidly increased to above 200 mg/L, followed by a slight decrease in concentration. Similar behaviour is observed in column D around 1.2 PV (unitless), where a similar increase to 90 mg/L was observed. This effect may have been a result of nitrogen conversion and the extended break between irrigation periods, allowing microorganisms in soil to recover.

A partitioning coefficient of $4*10^{-8}$ L/mg for column D was derived using total nitrogen data; column E's $5*10^{-8}$ L/mg was calculated using the ammoniacal-N data from column D. Values

used to calculate these include a soil density of 1780 kg/m^3 and a porosity of 35%. Soil E's favourable higher partitioning was drawn back by its toxic effect upon the soil and plant mediums, where visible soil "yellowing" and plant deaths were observed throughout. In comparison, column D had less partitioning potential, likely attributed to its weaker loading contaminant concentration, with little soil discolouration. Observations include slight "yellowing" of plant stems; however, this did not result in any plant deaths.

Based on the results from this experiment, it would be necessary to dilute raw landfill leachate by around 10 times or more before noticeable degradation of soil. More concentrated leachate could be used if best management practices are employed with regards to irrigation method, irrigated volume, and irrigation timing.

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Appendix A: Supplementary literature

Appendix A 1: Table 4.2. Soil limits and biosolids classification by contaminant levels, NZWWA. (2003).

[3] *All compost must have 30 days maturation pre-use.*

[4] *5 x 3 days at T ≥ 55°C plus time periods to reach 55°C after each turning.*

[5] *Based on representative samples before and after the reduction process (see section 7).*

Table 4.2: Soil limits and biosolids classification by contaminant levels

Parameter	Soil limit or ceiling concentrations[1] (mg/kg dry weight)	Biosolids limits[2]		
		Grade a max. concentration[3] (mg/kg dry weight)		Grade b max. concentration[3] (mg/kg dry weight)
Metals		*Until 31/12/12*	*After 31/12/12*	
Arsenic	20	20	20	30
Cadmium	1	3	1	10
Chromium	600	600	600	1500
Copper	100	300	100	1250
Lead	300	300	300	300
Mercury	1	2	1	7.5
Nickel	60	60	60	135
Zinc	300	600	300	1500
Organics				
DDT/DDD/DDE	0.5	0.5	0.5	0.5
Aldrin	0.02	0.02	0.02	0.2
Dieldrin	0.02	0.05	0.02	0.2
Chlordane	0.02	0.02	0.02	0.2
Heptachlor & Heptachlor epoxide	0.02	0.02	0.02	0.2
Hexachlorobenzene (HCB)	0.02	0.02	0.02	0.2
Hexachlorocyclohexane (Lindane)	0.02	0.02	0.02	0.2
Benzene hexachloride (BHC)	0.02	0.02	0.02	0.2
Total polychlorinated biphenyls (PCBs)	0.1	0.2	0.2	0.2
Total dioxin TEQ[4]	0.00001	0.00003	0.00003	0.00005

[1] *Refer to section 6.11 and Appendix III for advice on compliance.*

[2] *See section 7.5 for product monitoring requirements, and Table 7.2 for sampling frequencies. In the case of biosolids manufacturing facilities in existence prior to the publication of these* Guidelines *it is acceptable to use data up to 12 months old for the purposes of* product verification. *For the purposes of determining compliance at the 95 percentile for* routine sampling, *the age of the data set shall be no more than 2 years for metals and organochlorines and no more than 5 years for dioxins. This avoids the scenario of old data masking upward trends in contaminant concentration.*

[3] *Compliance against the biosolid limit values are to be 95 percentile from sampling results, with a maximum of 20% above the limits.*

Appendix A 2: Table III. Partitioning of applied N for Newington field site, Bowman, Clune, and Sutton (2002).

TABLE III

Partitioning of applied N (kg ha^{-1}) for the Newington field site (1998 and 1999)

	Nitrogen sink	Control	20%	50%	Undiluted
1998	Applied[a]	121	1216	3337	6082
	Leached[b]	82 (68)	97 (8)	331 (10)	446 (7)
	Immobilisation	24 (20)	559 (49)	1401 (42)	2099 (35)
	Turf uptake	10 (8)	37 (3)	171 (5)	221 (4)
	Gaseous loss [c]	5 (4)	523 (43)	1434 (43)	3316 (55)
1999	Applied [a]	139	1431[d]	3576[d]	7156[d]
	Leached[b]	78 (56)	115 (8)	386 (11)	781(11)
	Immobilisation	30 (22)	386 (27)[d]	866 (24)[d]	1973 (28)
	Turf uptake	19 (14)	57 (4)	173 (5)	292 (4)
	Gaseous loss [c]	12 (9)	873 (61)[d]	2151(60)[d]	4110 (57)[d]
Mean	Applied[a]	130	1324	3457	6619
	Leached[b]	80 (62)	106 (8)	359 (10)	624 (9)
	Immobilisation	27 (21)	473 (36)	1134 (33)	2036 (31)
	Turf uptake	15 (11)	47 (4)	172 (5)	257 (4)
	Gaseous loss[c]	9 (7)	698 (53)	1793 (52)	3713 (56)

Numbers in parentheses are percentages (%) of applied N.

* Data are the mean of triplicate samples.

[a] Includes N mineralisation (kg ha^{-1}).

[b] Comprises mineral N (NO_3^- NH_4^+, and NH_3) lost below root zone (600 mm).

[c] Derived from mass balance calculations and assume losses are due to denitrification and volatilisation.

[d] Significant at $P \leq 0.05$ for comparison between yearly N partitioning.

Table 3. Estimated annual leachate constituent deposition† rates on irrigation plots at the landfill in Section 12, T6N R13W, Ottawa County, Michigan, 2003–2006.

	Constituent deposition rates			
Constituent	2003	2004	2005	2006
Leachate, cm	32.2 (4.1)‡	5.0 (1.0)	8.6 (1.6)	7.2 (0.8)
Ag, g ha^{-1}	BD#	0.17 (0.05)	BD	BD
As, g ha^{-1}	46.0 (5.4)	7.9 (1.9)	15.7 (3.1)	9.2 (1.0)
Ba, g ha^{-1}	888 (112)	128 (27)	213 (37)	180 (23)
Cd, g ha^{-1}	0.05 (0.01)	BD	BD	BD
Cr, g ha^{-1}	105.5 (13.7)	15.8 (3.4)	25.5 (4.5)	17.8 (2.1)
Cu, g ha^{-1}	84.9 (16.3)	15.7 (3.4)	7.3 (1.3)	5.6 (0.6)
Hg, g ha^{-1}	0.32 (0.09)	BD	BD	0.06 (0.01)
Pb, g ha^{-1}	8.06 (1.16)	1.16 (0.23)	1.31 (0.23)	0.51 (0.05)
Se, g ha^{-1}	8.72 (1.61)	1.14 (0.39)	3.94 (0.69)	1.13 (0.13)
Zn, g ha^{-1}	134.4 (20.0)	26.4 (4.0)	20.8 (3.8)	15.0 (1.7)
SRP,§ g ha^{-1}	52.0 (5.9)	8.1 (2.7)	9.6 (1.4)	17.0 (2.0)
Total P, kg ha^{-1}	2.14 (0.23)	0.47 (0.09)	0.57 (0.09)	0.35 (0.04)
NO_3–N, kg ha^{-1}	9.18 (1.46)	1.67 (0.55)	3.45 (0.56)	2.13 (0.18)
SO_4–S, kg ha^{-1}	25.61 (3.15)	4.04 (0.97)	8.65 (1.79)	5.80 (0.64)
Ca, kg ha^{-1}	ND¶	52 (9)	259 (34)	82 (10)
Mg, kg ha^{-1}	ND	99 (19)	117 (18)	116 (13)
NH_4–N, kg ha^{-1}	961 (119)	173 (39)	337 (70)	195 (22)
TKN,§ kg ha^{-1}	ND	ND	312 (55)	251 (29)
TOC,§ kg ha^{-1}	1443 (204)	97 (24)	216 (41)	153 (17)
Cl, kg ha^{-1}	2648 (298)	494 (112)	703 (130)	502 (50)

† Deposition calculated from leachate concentrations and irrigation depths. Year means are not compared statistically because they largely reflect the variation in amounts of leachate applied and differences among years in solute concentrations (Table 1).

‡ Values are mean and sample standard deviation ($n = 3$ plots).

§ SRP, soluble reactive phosphorus; TKN, total Kjeldahl nitrogen; TOC, total organic carbon.

¶ ND, not determined; samples were not analyzed for Ca and Mg in 2003 or for TKN in 2003 and 2004.

BD, below detection.

Appendix B: Supplementary experimental work discussion

Appendix B1: Discussion of obstacles in determining method for bromide sampling .

Bromide column pore volume sampling process

The acquisition of a bromide sampling column (Hamilton PRP-x100, 10 um, 4.1 x 100 mm) was intended for use with the existing high performance liquid chromatograph (HPLC) equipment on campus (Hewlett Packard HPLC 1100 series).

Various obstacles were met when trying to sample bromide ions in pore volumes. The major one was that mobile phase and detection method of bromide ions varied with the HPLC model apparatus of use, concentration of ions in solution and bromide sampling column.

A detailed HPLC method by (Perrone et al., 2005) was developed according to EPA Method 321.8 for the determination of bromide and bromate in aqueous samples. This method used the identical PRP-x100 bromide sampling column with analytical conditions as follows:

- Column temperature, 35°C
- Flow rate, 1.5ml/min
- Mobile phase, 18 mM nitric acid and 34 mM ammonium hydroxide
- pH adjusted to 4.0 using dilute nitric acid and ammonium hydroxide

These variable parameters may differ for different analysed ions, concentrations and equipment used.

After extensive research, 2 methods of detection were viable, given the HPLC of use and bromide column. The previously mentioned (Perrone et al., 2005) method detected bromide through HPLC eluent via the ICP-MS system (ELan DRC II ICP-MS).

Other detection methods include indirect UV and conductivity detection methods; all with their respective varying analytical conditions.

(Perrone et al., 2005)'s method would have been the most ideal analysis method for analysis of bromide in pore volume; however access to an ICP-MS system was an issue. Indirect UV and conductivity both had their difficulties in procuring analysis equipment, also rendering these options unviable. Given the small amount of bromide samples for analysis, bromide sampling was eventually sent to Hills Laboratory for analysis; analysed as total bromine.

Appendix B 2: Organisational and Experimental Lessons.

This section details the lessons learnt whilst completing the thesis work. Lessons are summarised into 2 main categories: organisational and experimental lessons learnt. Most of this discussion reflects upon practices that could be done differently, should a project of similar calibre be undertaken again. This section only encompasses a small section of actual lessons learnt from this study.

Some organisational practices to improve on for future projects include:

To always take more photos than I think I need. Photos always help to explain situations better; at times I was caught up in the experiment and forgot to visually document every step of the experiment. An example of this includes the visual comparisons between column D and E's soil surface and vegetation degradation. Pictures have been added while flood-irrigating the columns, but I should have taken a final photo of the column (intact) before opening them for dissection.

Experimental improvements for future projects of this nature could involve immediate analysis of drainage upon collection. This would be the most ideal case, however it would drastically increase time spent due to preparation, calibration and wait times for tests to resolve (may not be viable in some cases). Tests conducted include: ammoniacal-N, nitrate-N, total nitrogen, pH, electrical conductivity and COD; where the most time consuming is COD analysis, requiring at least 2 hours for digestion, heating, resampling and cooling before testing.

Collected samples may degrade during storage dependent on storage conditions. The maximum set time allowed for sample storage before sampling was 2 weeks. Samples may continue to react with particulates drained from the column, or oxidize with air space in storage containers during this time. It may be worthwhile to thoroughly investigate techniques to minimizing the effects they have. This may include storing samples in containers with minimal air space for oxidation, and filtering drainage to eliminate any particulate matter at the drainage collection stage.

When conducting concentration tests (COD, nitrate-N, total nitrogen, ammoniacal-N), it may be beneficial to do a quick calculation beforehand to see whether drainage samples will test within the analysis limit of methods used. This helps to reduce the amount of under-ranged or

over-ranged samples conducted, provides more useful data, and reduces the expenditure of laboratory resources.

In future, it may be best to wait until I am ready for column experiments before I excavate them. In-situ columns were excavated from Kate Valley early on in the batch method stage; this left the columns sitting in the laboratory for about 2-3 months before they were ready for experimental use. During this time, periodic watering of the soil had to be conducted to avoid desiccation of soil (leading to fracture of soil media); this aided plant growth, extending roots into the soil column (undesirable). Earthworm activity also continued over this period, creating wormholes throughout the soil column; these holes may aid in preferential flow through the column. Excavating soil columns when they're ready for use would reduce these effects, and yield experimental results more in alignment with actual field conditions.

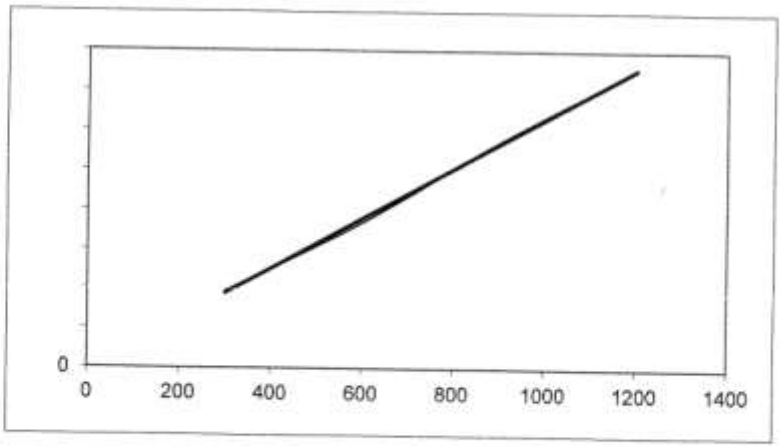
Appendix B 3: Chemical oxygen demand standard curve.

25/06/2007

Prepare 1200mg/l Cod Std 1.0213 gms dried KHP (100 °C 1hr)

mg/l	Abs 1	Abs 2
300	0.111	0.084
600	0.192	0.176
900	0.288	
1200	0.4	0.356

Std	mean
300	0.0975
600	0.184
900	0.286
1200	0.378



The above average absorbance values were used to create programme # 951 in the DR2000 spectrophotometer
A further range of digestions were done on standards and the following results obtained.

std	mg/l COD
300	308
600	610
900	912
1200	1199

Solutions
Sulphuric Acid Reagent
25.3g Silver Sulphate Ag_2SO_4 to 2.5 l sulphuric acid -stand for 48 hrs to dissolve
Solution A 10.216g $K_2Cr_2O_7$
167ml H_2SO_4
33.3g $HgSO_4$ mix in 500ml d.H_2O and dilute to 1 Litre
High Range Digestion solution
To 350ml of Sulphuric acid Reagent add 150ml of solution A in a water bath with care

Use 5ml of the High Range Digestion solution per test.

Appendix C: Batch test data and graphs

Appendix C 1. Sampled initial pH, COD and conductivity values in leachate.

Analysis Date	Dilution, Times	Conductivity, µS/cm	pH	COD, mg/L
15-Jun-12	0	5300	7.72	879
31-Oct-12	5	3280	7.68	431
8-Feb-13	5	2874	7.99	429
31-Oct-12	10	1674	7.55	226
31-Oct-12	20	915	7.56	119
8-Feb-13	20	766	7.75	87
8-Feb-13	35	443.5	7.65	42
8-Feb-13	50	106	6.87	17.58
15-Jun-12	control	1.9	6.37	0

Appendix C 2. Calculated initial and sampled equilibrium pH, EC and COD.

Analysis Date	Dilution	Soil Type, cm	Projected initial cond., µS/cm	Equilibrium electrical conductivity, µS/cm	Projected initial pH	Equilibrium pH	Projected initial COD, mg/L	Equilibrium COD, mg/L	mg of COD adsorbed/mg of soil
15-Jun-12	0	0-20	5300	3593	7.72	8.37	879	703	0.000411
15-Jun-12	0	0-20	5300	3553	7.72	8.29	879	750	0.000301
1-Dec-12	5	0-20	3077	1933	7.835	6.61	430	1650	0.002847
1-Dec-12	5	0-20	3077	2356	7.835	6.94	430	1107	0.00158
8-Feb-13	5	0-20					431	1888	0.0034
15-Jun-12	10	0-20	1674	2412	7.55	6.22	226		0.000527
15-Jun-12	10	0-20	1674	2290	7.55	6.48	226	110	0.000271
1-Dec-12	20	0-20	840.5	936	7.655	5.28	103	912	0.001888
1-Dec-12	20	0-20	840.5	789	7.655	5.83	103	979	0.002044
8-Feb-13	35	0-20					42		0.000098
1-Dec-12	50	0-20	106	773	6.87	4.8	17.58	1824	0.004215
1-Dec-12	50	0-20	106	771	6.87	4.84	17.58	1158	0.002661

15-Jun-12	control	0-20	1.9	194.6	7.72	8.02	0	80	0.000187
15-Jun-12	control	0-20	1.9	174.4	7.72	7.54	0	60	0.00014
1-Dec-12	control	0-20	1.9	616	7.72	4.62	0	1648	0.003845
1-Dec-12	control	0-20	1.9	622	7.72	4.61	0	1790	0.004177
1-Dec-12	5	20-40	3077	2344	7.835	6.65	430	964	0.001246
1-Dec-12	5	20-40	3077	2339	7.835	7.63	430	844	0.000966
8-Feb-13	5	20-40					430	1608	0.002749
1-Dec-12	20	20-40	840.5	938	7.655	5.39	103	913	0.00189
1-Dec-12	20	20-40	840.5	716	7.655	6.42	103	1368	0.002952
8-Feb-13	35	20-40					42	1118	0.002511
1-Dec-12	50	20-40	106	577	6.87	5.08	17.58	1386	0.003193
1-Dec-12	50	20-40	106	565	6.87	5.1	17.58	1224	0.002815
1-Dec-12	control	20-40	1.9	411	7.72	4.81	0	1586	0.003701
1-Dec-12	control	20-40	1.9	409	7.72	4.82	0	1876	0.004377
15-Jun-12	0	40-60	5300	3531	7.72	8.17	879	710	0.000394
15-Jun-12	0	40-60	5300	3516	7.72	8.12	879	690	0.000441
1-Dec-12	5	40-60	3077	2304	7.835	6.88	430	1910	0.003453
1-Dec-12	5	40-60	3077	2409	7.835	7.19	430	866	0.001017
8-Feb-13	5	40-60					430	1100	0.001563
15-Jun-12	10	40-60	1674	2419.5	7.55	6.73	226	89	0.00032
15-Jun-12	10	40-60	1674	2407	7.55	6.92	226	74	0.000355
15-Jun-12	10	40-60	1674	2391.5	7.55	7.11	226	86	0.000327
1-Dec-12	20	40-60	840.5	785	7.655	5.8	103	1292	0.002774
1-Dec-12	20	40-60	840.5	713	7.655	6.56	103	1126	0.002387
8-Feb-13	35	40-60					42	823	0.001822
8-Feb-13	35	40-60					42	870	0.001932
8-Feb-13	35	40-60					42	847	0.001878
8-Feb-13	35	40-60					42	859	0.001906
8-Feb-13	35	40-60					42	832	0.001843
1-Dec-12	50	40-60	106	525	6.87	5.39	17.58	1200	0.002759
1-Dec-12	50	40-60	106	463	6.87	5.39	17.58	1176	0.002703
15-Jun-12	control	40-60	1.9	516	7.72	8.15	0	60	0.00014
15-Jun-12	control	40-60	1.9	561	7.72	7.85	0		0

1-Dec-12	control	40-60	1.9	340	7.72	5.02	0	1744	0.004069
1-Dec-12	control	40-60	1.9	336	7.72	5.01	0	1316	0.003071

Appendix C 3. Sampled initial ammonia and total nitrogen values in leachate.

Analysis Date	Dilution, Times	Ammonia, mg of NH_3-N/L	Total Nitrogen, mg of Total-N/L
15-Jun-12		1070	1100
31-Oct-12	5	120	220
31-Oct-12	5	123	
31-Oct-12	5	176	
15-Jun-12	10		110
31-Oct-12	10	87.5	117
31-Oct-12	10	89	108
31-Oct-12	20	49	63
31-Oct-12	20	48	65
31-Oct-12	20	45.9	25
31-Oct-12	35	24.9	13
31-Oct-12	50	21.4	22

Appendix C 4. Calculated initial and sampled equilibrium ammonia, nitrate and total nitrogen.

Dilution	Soil Type, cm	Projected initial Nitrate, mg of NO_3^--N/L	Equilibrium Nitrate, mg of NO_3^--N/L	Projected initial Ammonia, mg of NH_3-N/L	Equilibrium Ammonia, mg of NH_3-N/L	mg of Ammonia adsorbed/mg of soil	Projected initial Total nitrogen, mg of Total-N/L	Equilibrium Total nitrogen, mg of Total-N/L
0	0-20	0.02	11.3					
0	0-20	0.02	13.2					
0	0-20	0.02	10	1070	2.6	0.0024906	1100	51
0	0-20	0.02	5.3	1070	4.3	0.002486633	1100	59
3	0-20			220.0402	182	8.87604E-05		
4	0-20			173.4014	147.6	6.02034E-05		
5	0-20	0.02	11.5	120	79.5	0.0000945	220	192

5	0-20	0.02		1.8	120		105	0.000035	220	204
5	0-20				120		96	0.000056		
5	0-20				120		79.5	0.0000945		
5	0-20				120		105	0.000035		
5	0-20				120		96	0.000056		
6	0-20				123.9507		91.2	7.64184E-05		
8	0-20				97.6787		53.2	0.000103784		
10	0-20	0.02	18.7		88.25	12.1		0.000177683		
10	0-20	0.02	4.3		88.25	10.6		0.000181183		
20	0-20	0.02		7	45.74099		23.5	5.18956E-05	45.47217	148
20	0-20	0.02		4.1	45.74099		20.3	5.93623E-05	45.47217	129
20	0-20				45.74099		23.5	5.18956E-05		
20	0-20				45.74099		20.3	5.93623E-05		
35	0-20				28.77862		16.8	2.79501E-05		
35	0-20				28.77862		16.8	2.79501E-05		
50	0-20	0.02		7.9	21.41959		9.5	2.78124E-05	15.1432	71
50	0-20	0.02		8.5	21.41959		11.2	2.38457E-05	15.1432	75
50	0-20				21.41959		9.5	2.78124E-05		
50	0-20				21.41959		11.2	2.38457E-05		
Control	0-20	0	10.2		0	1		-2.33333E-06		
Control	0-20	0	8		0	1.1		-2.56667E-06		
0	20-40	0.02		4.4	1070		1.9	0.002492233	1100	40
0	20-40	0.02		4.2	1070		2.1	0.002491767	1100	47
3	20-40				220.0402		184.4	8.31604E-05		
4	20-40				173.4014		106	0.00015727		
5	20-40	0.02		27	120		105	0.000035	220	180
5	20-40	0.02		1.5	120		108	0.000028	220	172
5	20-40				120		102	0.000042		
5	20-40				120		105	0.000035		
5	20-40				120		108	0.000028		
5	20-40				120		102	0.000042		
6	20-40				123.9507		76.4	0.000110952		
8	20-40				97.6787		56.4	9.6317E-05		

20	20-40	0.02		6.6	45.74099		22.9	5.32956E-05	45.47217	164
20	20-40	0.02		5	45.74099		17	6.70623E-05	45.47217	112
20	20-40				45.74099		22.9	5.32956E-05		
20	20-40				45.74099		17	6.70623E-05		
35	20-40				28.77862		13.5	3.56501E-05		
35	20-40				28.77862		13.5	3.56501E-05		
50	20-40	0.02		3	21.41959		7.6	3.22457E-05	15.1432	69
50	20-40	0.02		3	21.41959		7.8	3.17791E-05	15.1432	55
50	20-40				21.41959		7.6	3.22457E-05		
50	20-40				21.41959		7.8	3.17791E-05		
0	40-60	0.02	11.4		1070	5.4		0.002484067		
0	40-60	0.02	11							
0	40-60	0.02		3.6	1070		1.6	0.002492933	1100	46
0	40-60	0.02		4	1070		1.4	0.0024934	1100	29
3	40-60				220.0402		202	4.20937E-05		
4	40-60				173.4014		133.6	9.287E-05		
5	40-60	0.02		3.4	120		87	0.000077	220	216
5	40-60	0.02		0.9	120		111.75	0.00001925	220	212
5	40-60				120		93.2	6.25333E-05		
5	40-60				120		87	0.000077		
5	40-60				120		111.75	0.00001925		
5	40-60				120		93.2	6.25333E-05		
6	40-60				123.9507		82.8	9.60184E-05		
8	40-60				97.6787		62.4	8.2317E-05		
10	40-60	0.02	4		88.25	12.8		0.00017605		
10	40-60	0.02	3.9							
10	40-60	0.02	3.1		88.25	12.9		0.000175817		
20	40-60	0.02		3.1	45.74099		33.6	2.8329E-05	45.47217	169
20	40-60	0.02		7.7	45.74099		18.8	6.28623E-05	45.47217	117
20	40-60				45.74099		33.6	2.8329E-05		
20	40-60				45.74099		18.8	6.28623E-05		
35	40-60				28.77862		11.3	4.07835E-05		
35	40-60				28.77862		12.2	3.86835E-05		

35	40-60				28.77862		12.2	3.86835E-05		
35	40-60				28.77862		12.1	3.89168E-05		
35	40-60				28.77862		17	2.74835E-05		
35	40-60				28.77862		11.3	4.07835E-05		
35	40-60				28.77862		12.2	3.86835E-05		
35	40-60				28.77862		12.2	3.86835E-05		
35	40-60				28.77862		12.1	3.89168E-05		
35	40-60				28.77862		17	2.74835E-05		
50	40-60	0.02		5.1	21.41959		6.9	3.38791E-05	15.1432	43
50	40-60	0.02		3.8	21.41959		6.3	3.52791E-05	15.1432	57
50	40-60				21.41959		6.9	3.38791E-05		
50	40-60				21.41959		6.3	3.52791E-05		
Control	40-60	0	30.3		0	0		0		
Control	40-60	0	5.8		0	0.6		-0.0000014		

Appendix D: Column test data and graphs

Appendix D 1: 10x raw leachate dilution column experiment data.

										INITIAL 10X VALUES:			8.1	1136	135	111	0.6	307
Day	Date	Irrigation Time	Leachate Collection Time	Time Stamp	Cumulative Time, hh:mm:ss	Column Flow Rate, ml/hr	Code	Weight of Analysis Sample Collected, g	Drainage Volume Weight, g	Total Pore Volume, ml	Cumulative pore volume, Liters	Pore volume, unitless	pH	Conductivity (uS/cm)	Total Nitrogen, mg/L	Ammoniacal-N, mg/L	Nitrate-N, mg/L	COD, mg/L
1	26-Jul	**2:00 p.m.**		26/07/2013 14:00														
1	26-Jul		4:50 PM - 5:00 PM	26/07/2013 18:00	4:00:00	197.89	**D1.1**	35.68					6.83	450	9	0.5	9	79
									558	594	0.594	0.026						
			7:45 PM - 8:05 PM	26/07/2013 20:05	6:05:00		**D1.2**	12.41			0.001	0.000	7.21	570		1.8	9	95
									606	606	0.607	0.027						
2	27-Jul	**3:30 p.m.**		27/07/2013 15:30	25:30:00						0.607	0.027						
2	27-Jul		3:20 p.m.	27/07/2013 15:20	25:20:00				59	59	0.666	0.029						
2	27-Jul		7:30 PM - 7:40 PM	27/07/2013 19:40	29:40:00	207.59	**D2.1**	27.97			0.666	0.029	7.15	494.5		3	13	103
									837	865	1.531	0.067						
			11:00 PM - 11:30 PM	27/07/2013 23:30	33:30:00		**D2.2**	9.14			1.531	0.067	7.86	477.3		3.4	10	134
									491	500	2.031	0.089						
3	28-Jul	**4:30 p.m.**		28/07/2013 16:30	50:30:00						2.031	0.089						
3	28-Jul		4:30 PM - 4:45 PM	28/07/2013 16:45	50:45:00		**D3.0**	35.88			2.031	0.089	7.76	502		2.2	6	64
									30	66	2.097	0.092						
			7:30 PM - 7:40 PM	28/07/2013 19:40	53:40:00	181.22	**D3.1**	34.67			2.097	0.092	7.71	563		5.6	12	106
									509	544	2.640	0.115						
			11:30 PM - 11:45 PM	28/07/2013 23:45	57:45:00	197.76	**D3.2**	14.03			2.640	0.115	7.97	548		8.7	6	125
									777	791	3.431	0.150						
6	31-Jul	**10:00 a.m.**		31/07/2013 10:00	116:00:00						3.431	0.150						
6	31-Jul		9:50 a.m.	31/07/2013 9:50	115:50:00				45	45	3.476	0.152						
6	31-Jul		1:30 PM - 1:45 PM	31/07/2013 13:45	119:45:00	156.89	**D6.1**	32.34			3.476	0.152	7.77	623	10	7.6	11	163
									556	588	4.065	0.178						
			3:30 PM - 3:45 PM	31/07/2013 15:45	121:45:00	216.81	**D6.2**	28.62			4.065	0.178	7.73	592		8.4	10	113
									405	434	4.498	0.197						
9	3-Aug	**3:30 p.m.**		3/08/2013 15:30	193:30:00						4.498	0.197						
9	3-Aug		3:10 p.m.	3/08/2013 15:10	193:10:00				331	331	4.829	0.211						
9	3-Aug		5:50 PM - 6:00 PM	3/08/2013 18:00	196:00:00	150.34	**D9.1**	20.02			4.829	0.211	7.71	631		6.8	19	115
									431	451	5.280	0.231						
10	4-Aug		12:05 AM - 12:30 AM	4/08/2013 0:30	202:30:00	136.11	**D9.2**	7.73			5.280	0.231	7.9	618		8.6	22	124
									877	885	6.165	0.269						
10	4-Aug		3:30 p.m.	4/08/2013 15:30	217:30:00				14.63	15	6.180	0.270						
13	7-Aug	**12:30 p.m.**		7/08/2013 12:30	286:30:00						6.180	0.270						

13	7-Aug		12:30 PM - 12:40 PM	7/08/2013 12:40	286:40:00		**D13.1**	26.85			6.180	0.270	7.47	620	15	4.3	6.4	80
									300	327	6.506	0.284						
			6:05 PM - 6:15PM	7/08/2013 18:15	292:15:00	119.56	**D13.2**	17.46			6.506	0.284	7.52	670		7.4	7	92
									676	693	7.200	0.315						
14	8-Aug	**2:30 p.m.**		8/08/2013 14:30	312:30:00						7.200	0.315						
14	8-Aug		2:30 p.m.	8/08/2013 14:30	312:30:00				422	422	7.622	0.333						
14	8-Aug		5:50 PM - 6:00 PM	8/08/2013 18:00	316:00:00	121.21	**D14.1**	20.23			7.622	0.333	7.63	703		6.1	8	77
									404	424	8.046	0.352						
			11:10 PM - 11:30 PM	8/08/2013 23:30	321:30:00	113.71	**D14.2**	23.41			8.046	0.352	7.75	712		7.1	14.6	81
									602	625	8.672	0.379						
15	9-Aug	**12:30 p.m.**		9/08/2013 12:30	334:30:00						8.672	0.379						
15	9-Aug		12:30 p.m.	9/08/2013 12:30	334:30:00				369	369	9.041	0.395						
15	9-Aug		5:00 PM - 5:10 PM	9/08/2013 17:10	339:10:00	97.72	**D15.1**	21.84			9.041	0.395	7.87	737	20	6.7	12.8	85
									457	479	9.519	0.416						
			10:30 PM - 11:00 PM	9/08/2013 23:00	345:00:00	91.32	**D15.2**	18.91			9.519	0.416	7.88	745		7.1	14	82
									529	548	10.067	0.440						
17	11-Aug		6:00 p.m.	11/08/2013 18:00	388:00:00				406	406	10.473	0.458						
18	12-Aug	**12:00 a.m.**		12/08/2013 0:00	394:00:00						10.473	0.458						
18	12-Aug	**3:30 p.m.**		12/08/2013 15:30	409:30:00						10.473	0.458						
18	12-Aug		3:30 PM - 3:45 PM	12/08/2013 15:45	409:45:00	87.54	**D18.1**	45.84			10.473	0.458	8.06	1470	21	7.3	21.2	125
									1311	1357	11.830	0.517						
19	13-Aug	**5:00 p.m.**		13/08/2013 17:00	435:00:00						11.830	0.517						
19	13-Aug		5:00 PM - 5:20 PM	13/08/2013 17:20	435:20:00	57.42	**D19.1**	26.7			11.830	0.517	7.82	1496		4.7		127
									1437.55	1464	13.294	0.581						
			9:00 PM - 9:20 PM	13/08/2013 21:20	439:20:00	76.94	**D19.2**	32.41			13.294	0.581	7.76	1525		8.9		120
									275.33	308	13.602	0.594						
19	13-Aug	**10:00 p.m.**		13/08/2013 22:00	440:00:00						13.602	0.594						
20	14-Aug		10:15 AM - 10:30 AM	14/08/2013 10:30	452:30:00	85.98	**D20.1**	30.78			13.602	0.594	7.79	1524		9.4	9.6	105
									1044	1075	14.677	0.641						
			2:10 PM - 2:30 PM	14/08/2013 14:30	456:30:00		**D20.2**	24.03			14.677	0.641	7.95	1512	35	9.3		114
									251	275	14.952	0.653						
21	15-Aug	**3:00 p.m.**		15/08/2013 15:00	481:00:00						14.952	0.653						
21	15-Aug		3:00 p.m.	15/08/2013 15:00	481:00:00				538.8	539	15.490	0.677						
21	15-Aug		9:00 PM - 9:10 PM	15/08/2013 21:10	487:10:00	92.96	**D21.1**	22.75			15.490	0.677	7.99	1404				108
									535	557.75	16.048	0.701						
23	17-Aug	**3:30 p.m.**		17/08/2013 15:00	529:00:00						16.048	0.701						

23	17-Aug		2:50 PM - 3:00 PM	17/08/2013 15:30	529:30:00					828	828	16.876	0.737								
23	17-Aug		6:00 p.m. - 6:20 p.m.	17/08/2013 18:20	532:20:00	65.64	**D23.1**	41.36				16.876	0.737	7.79	1463			21.8		123	
										155.55	196.91	17.073	0.746								
			11:00 p.m. - 11:30 p.m.	17/08/2013 23:30	537:30:00	64.14	**D23.2**	44.88				17.073	0.746	7.93	1056	17				106	
										275.84	320.72	17.394	0.760								
24	18-Aug		1:30 a.m.	18/08/2013 1:30	539:30:00					152.48	152.48	17.546	0.767								
25	19-Aug		4:30 p.m.	19/08/2013 16:30	578:30:00					703	703	18.249	0.797								
25	19-Aug	**4:30 p.m.**		19/08/2013 16:30	578:30:00							18.249	0.797								
25	19-Aug		8:00 p.m. - 8:20 p.m.	19/08/2013 20:20	582:20:00		**D25.1**	22.33				18.249	0.797	7.77	1555			8		110	
											22.33	18.272	0.798								
27	21-Aug		10:00 a.m.	21/08/2013 10:00	620:00:00					1388.6	1388.6	19.660	0.859								
27	21-Aug	**10:00 a.m.**		21/08/2013 10:00	620:00:00							19.660	0.859								
27	21-Aug		1:50 p.m. - 2:00 p.m.	21/08/2013 14:00	624:00:00	64.37	**D27.1**	16.47				19.660	0.859	7.92	1211		11.6	22.4		120	
										241	257.47	19.918	0.870								
28	22-Aug		11:30 p.m.	22/08/2013 23:30	657:30:00					1152.73	1152.73	21.070	0.921								
29	23-Aug	**6:30 p.m.**		23/08/2013 18:30	676:30:00							21.070	0.921								
30	24-Aug		2:30 a.m. - 2:50 a.m.	24/08/2013 2:50	684:50:00	64.58	**D30.1**	34.59				21.070	0.921	7.77	1660		12.3	23.6		95	
										514.38	548.97	21.619	0.945								
31	25-Aug		3:30 p.m.	25/08/2013 15:30	721:30:00					828.53	828.53	22.448	0.981								
31	25-Aug	**3:30 p.m.**		25/08/2013 15:30	721:30:00							22.448	0.981								
31	25-Aug		8:30 p.m. - 8:50 p.m.	25/08/2013 20:50	726:50:00	59.00	**D31.1**	39.75				22.448	0.981	7.83	1697	47				116	
										284.73	324.48	22.772	0.995								
32	26-Aug		1:00 a.m. - 1:30 a.m.	26/08/2013 1:30	731:30:00		**D32.1**	44.19				22.772	0.995	8.05	1685		13.7	22		118	
										227.42	271.61	23.044	1.007								
33	27-Aug		1:30 a.m.	27/08/2013 1:30	755:30:00					812.6	812.6	23.857	1.043								
33	27-Aug	**2:30 p.m.**		27/08/2013 14:30	768:30:00							23.857	1.043								
33	27-Aug		8:00 p.m. - 8:30 p.m.	27/08/2013 20:30	774:30:00	53.58	**D33.1**	26.42				23.857	1.043	7.44	1696			19.3		111	
										295.06	321.48	24.178	1.057								
34	28-		10:00 p.m.	28/08/2013 22:00	800:00:00					1016	1016	25.194	1.101								

	Aug																		
35	29-Aug	**3:00 p.m.**											25.194	1.101					
35	29-Aug		7:30 p.m. - 8:00 p.m.	29/08/2013 20:30	822:30:00		**D35.1**	28.58				25.194	1.101	7.45	1644	55	0.5	29	521
									459.196	487.776		25.682	1.122						
37	31-Aug		7:00 p.m.	31/08/2013 19:00	869:00:00				1037.83	1037.83		26.720	1.168						
37	31-Aug	**7:00 p.m.**										26.720	1.168						
38	1-Sep		1:00 a.m. - 1:30 a.m.	1/09/2013 1:00	875:00:00	53.13	**D37.1**	25.34				26.720	1.168	7.43	1650		0.7		40
									320	345.34		27.065	1.183						
39	2-Sep		4:00 p.m.	2/09/2013 16:00	914:00:00				1066	1066		28.131	1.229						
39	2-Sep	**4:00 p.m.**										28.131	1.229						
39	2-Sep		7:30 p.m. - 8:00 p.m.	2/09/2013 20:30	918:30:00	60.65	**D39.1**	40.59				28.131	1.229	7.41	1587		0.3	21.7	121
									202	242.59		28.374	1.240						
41	4-Sep	**10:30 a.m.**										28.374	1.240						
41	4-Sep		10:30 a.m. - 11:00 a.m.	4/09/2013 11:00	957:00:00		**D41.1**	41.71				28.374	1.240	7.51		89	0.4		126
									1161	1202.71		29.576	1.292						
41	4-Sep		11 p.m.	4/09/2013 23:00	969:00:00	55.92			671	671		30.247	1.322						
42	5-Sep		11 a.m.	5/09/2013 11:00	981:00:00				564	564		30.811	1.346						
43	6-Sep	**6:30 p.m.**										30.811	1.346						
43	6-Sep		6:30 p.m.	6/09/2013 18:30	1012:30:00		SPILLED					30.811	1.346						
									100	100		30.911	1.351						
45	8-Sep		10:00:00 p.m.	8/09/2013 22:00	1064:00:00				1410	1410		32.321	1.412						
45	8-Sep	**10:00 p.m.**										32.321	1.412						
46	9-Sep		3:00 p.m. - 10:00 p.m.	9/09/2013 22:00	1088:00:00		**D46.1**	296				32.321	1.412	7.25	1583	66	2.2	58.2	349
									878	1174		33.495	1.464						
47	10-Sep	**3:30 p.m.**										33.495	1.464						
47	10-Sep		3:30 p.m.	10/09/2013 15:30	1105:30:00				163	163		33.658	1.471						
47	10-Sep		7:30 p.m. - 8:00 p.m.	10/09/2013 20:00	1110:00:00		**D47.1**	48.75				33.658	1.471	7.1	1695		0	50.2	286
									161	209.75		33.868	1.480						
49	12-Sep	**12:00 p.m.**										33.868	1.480						
51	14-Sep		10:00:00 p.m.	14/09/2013 22:00	1208:00:00				1214	1214		35.082	1.533						
51	14-Sep	**11:00 p.m.**										35.082	1.533						
51	14-Sep		11:00 p.m. - 11:30 p.m.	14/09/2013 23:30	1209:30:00		**D52.1**	27.61				35.082	1.533	7.06	1676	65	1.5	57.8	226
									1374	1401.61		36.484	1.594						
52	15-Sep		10:00:00 p.m.	15/09/2013 22:00	1232:00:00	55.30			1272	1272		37.756	1.650						
53	16-Sep	**4:15 p.m.**	**Started collecting 500ml for Hills Lab**									37.756	1.650						
53	16-Sep		4:15:00 p.m.	16/09/2013 16:15	1250:15:00				79	79		37.835	1.653						
54	17-Sep		3:30 p.m.	17/09/2013 15:30	1273:30:00	53.09	***D54.1**		1221	1221		39.056	1.707	6.98	1702	61	0	37.2	128
56	19-Sep	**10:30 a.m.**										39.056	1.707						
56	19-Sep		10:30:00 a.m.	19/09/2013 10:30	1316:30:00				217	217		39.273	1.716						

| | | |

Appendix D 2: 2x raw leachate dilution column experiment data.

										INITIAL 2X VALUES:			7.89	8.14	675	553	3	1535
Day	Date	Irrigation Time	Leachate Collection Time	Time Stamp	Cumulative Time, hh:mm:ss	Column Flow Rate, ml/hr	Code	Weight of Analysis Sample Collected, g	Pore Volume Weight, g	Total Pore Volume, ml	Cumulative pore volume, Liters	Pore volume, unitless	pH	Conductivity (uS/cm)	Total Nitrogen, mg/L	Ammoniacal-N, mg/L	Nitrate-N, mg/L	COD, mg/L
1	15-Aug	**3:00 p.m.**		15/08/2013 15:00	72:00:00													
1	15-Aug		9:00 p.m. - 9:10 p.m.	15/08/2013 21:10	6:10:00	43.46	**E1.1**	11.09							UR	0.1		
									254	265.09	0.265	0.012						
3	17-Aug		3:00 p.m.	17/08/2013 15:00	48:00:00				1009	1009	1.274	0.056						
3	17-Aug	**3:30 p.m.**		17/08/2013 15:30	48:30:00						1.274	0.056						
3	17-Aug		6:00 p.m. - 6:20 p.m.	17/08/2013 18:20	51:20:00		**E3.1**	36.78			1.274	0.056	7.89	904	1	0.8	4.5	42
									655.21	691.99	1.966	0.086						
			11:00 p.m. - 11:30 p.m.	17/08/2013 23:30	56:30:00	58.01	**E3.2**	40.41			1.966	0.086	7.94	983		1.6	5.5	90
									249.64	290.05	2.256	0.099						
4	18-Aug		1:30 a.m.	18/08/2013 1:30	58:30:00				145.04	145.04	2.401	0.105						
5	19-Aug		4:30 p.m.	19/08/2013 16:30	97:30:00				734	734	3.135	0.137						
5	19-Aug	**4:30 p.m.**		19/08/2013 16:30	97:30:00						3.135	0.137						
5	19-Aug		8:00 p.m. - 8:20 p.m.	19/08/2013 20:20	101:20:00		**E5.1**	25.8			3.135	0.137	8.17	1164	11	2.4	5	86
										25.8	3.161	0.138						
7	21-Aug		10:00 a.m.	21/08/2013 10:00	139:00:00				1285.85	1285.85	4.447	0.194						
7	21-Aug	**10:00 a.m.**		21/08/2013 10:00	139:00:00						4.447	0.194						
7	21-Aug		1:50 p.m. - 2:00 p.m.	21/08/2013 14:00	143:00:00	40.05	**E7.1**	9.19			4.447	0.194	7.77			2.9		144
									151	160.19	4.607	0.201						
8	22-Aug		11:30 p.m.	22/08/2013 23:30	176:30:00				1202.17	1202.17	5.809	0.254						
9	23-Aug	**6:30 p.m.**		23/08/2013 18:30	195:30:00						5.809	0.254						
10	24-Aug		2:30 a.m. - 2:50 a.m.	24/08/2013 2:50	203:50:00	55.40	**E10.1**	27.34			5.809	0.254	7.44	3245	23	14.7	3	266
									443.56	470.9	6.280	0.274						
11	25-Aug		3:30 p.m.	25/08/2013 15:30	240:30:00				897.92	897.92	7.178	0.314						
11	25-Aug	**3:30 p.m.**		25/08/2013 15:30	240:30:00						7.178	0.314						
11	25-Aug		8:30 p.m. - 8:50 p.m.	25/08/2013 20:50	245:50:00	45.75	**E11.1**	21.7			7.178	0.314	7.45	3514		3.6	4.5	358
									229.95	251.65	7.430	0.325						
12	26-Aug		1:00 a.m. - 1:30 a.m.	26/08/2013 1:30	250:30:00		**E12.1**	31.53			7.430	0.325	7.48	3766		4.1	3.5	450
									157.39	188.92	7.619	0.333						
13	27-Aug		1:30 a.m.	27/08/2013 1:30	274:30:00				843.38	843.38	8.462	0.370						
13	27-Aug	**2:30 p.m.**		27/08/2013 14:30	287:30:00						8.462	0.370						
13	27-Aug		8:00 p.m. - 8:30 p.m.	27/08/2013 20:30	293:30:00	56.19	**E13.1**	25.31			8.462	0.370	7.32	4556	4	UR	4	430
									311.82	337.13	8.799	0.385						
14	28-Aug		10:00 p.m.	28/08/2013 22:00	319:00:00				816	816	9.615	0.420						
15	29-Aug	**3:00 p.m.**									9.615	0.420						
15	29-Aug		7:30 p.m. - 8:00 p.m.	29/08/2013 20:30	341:30:00		**E15.1**	17.45			9.615	0.420	6.22	3624	25	4.4	2	244

										0	17.45	9.633	0.421						
17	31-Aug		7:00 p.m.	31/08/2013 19:00	388:00:00					1159.91	1159.91	10.792	0.472						
17	31-Aug	**7:00 p.m.**										10.792	0.472						
18	1-Sep		1:00 a.m. - 1:30 a.m.	1/09/2013 1:00	394:00:00	46.98	**E17.1**	22.4				10.792	0.472	6.81	4382		51	4.4	418
										283	305.4	11.098	0.485						
19	2-Sep		4:00 p.m.	2/09/2013 16:00	433:00:00					1087	1087	12.185	0.532						
19	2-Sep	**4:00 p.m.**										12.185	0.532						
19	2-Sep		7:30 p.m. - 8:00 p.m.	2/09/2013 20:30	437:30:00	47.63	**E19.1**	21.95				12.185	0.532	7.47	4177		32.2	1.6	272
										168.58	190.53	12.375	0.541						
21	4-Sep	**10:30 a.m.**										12.375	0.541						
21	4-Sep		10:30 a.m. - 11:00 a.m.	4/09/2013 11:00	476:00:00		**E21.1**	13.71				12.375	0.541	7.53		63	31.8	2.8	816
										1191	1204.71	13.580	0.593						
21	4-Sep		11 p.m.	4/09/2013 23:00	488:00:00	41.74				480	480	14.060	0.614						
22	5-Sep		11 a.m.	5/09/2013 11:00	500:00:00	34.58				415	415	14.475	0.633						
23	6-Sep	**6:30 p.m.**										14.475	0.633						
23	6-Sep		6:30 p.m.	6/09/2013 18:30	531:30:00		**XXX**					14.475	0.633						
										523	523	14.998	0.655						
25	8-Sep		10:00:00 p.m.	8/09/2013 22:00	583:00:00					1379	1379	16.377	0.716						
25	8-Sep	**10:00 p.m.**										16.377	0.716						
26	9-Sep		3:00 p.m. - 10:00 p.m.	9/09/2013 22:00	607:00:00	32.79	**E26.1**	243				16.377	0.716	7.75	4466	59	29.2	2.4	934
										544	787	17.164	0.750						
27	10-Sep	**3:30 p.m.**										17.164	0.750						
27	10-Sep		3:30 p.m.	10/09/2013 15:30	624:30:00					303	303	17.467	0.763						
27	10-Sep		7:30 p.m. - 8:00 p.m.	10/09/2013 20:00	629:00:00	25.32	**E27.1**	36.61				17.467	0.763						
										90	126.61	17.594	0.769						
29	12-Sep	**12:00 p.m.**										17.594	0.769						
31	14-Sep		10:00:00 p.m.	14/09/2013 22:00	727:00:00					922	922	18.516	0.809						
31	14-Sep	**11:00 p.m.**										18.516	0.809						
31	14-Sep		11:00 p.m. - 11:30 p.m.	14/09/2013 23:30	728:30:00		**E32.1**	18.8				18.516	0.809	7.44	4930	84	55.8	3.6	384
										1192	1210.8	19.726	0.862						
32	15-Sep		10:00:00 p.m.	15/09/2013 22:00	751:00:00					523	523	20.249	0.885						
33	16-Sep	**4:15 p.m.**	**Started collecting 500ml for Hills Lab**									20.249	0.885						
33	16-Sep		4:15:00 p.m.	16/09/2013 16:15	769:15:00					439	439	20.688	0.904						
34	17-Sep		3:30 p.m.	17/09/2013 15:30	792:30:00	27.48	***E34.1**			632	632	21.320	0.932	7.33	4707	90	65.6	1.6	432
36	19-Sep	**10:30 a.m.**										21.320	0.932						
36	19-Sep		10:30:00 a.m.	19/09/2013 10:30	835:30:00					1287	1287	22.607	0.988						
38	21-Sep	**7:00 p.m.**										22.607	0.988						
38	21-Sep		7:00:00 p.m.	21/09/2013 7:00	880:00:00					1393	1393	24.000	1.049						
40	23-Sep	**8:00 p.m.**										24.000	1.049						
40	23-Sep		8:00:00 p.m.	23/09/2013 8:00	929:00:00					1354	1354	25.354	1.108						
41	24-Sep	**10:00 p.m.**										25.354	1.108						
41	24-Sep		10:00 p.m. - 10:30 p.m.	24/09/2013 22:30	967:30:00		**E41**	42.58				25.354	1.108	7.56	5970		92	49.6	751
										922.54	965.12	26.320	1.150						
42	25-Sep		6:30:00 p.m.	25/09/2013 18:30	987:30:00	20.15				403	403	26.723	1.168						

43	26-Sep	**6:30 p.m.**										26.723	1.168						
43	26-Sep		3:00 p.m. - 3:30 p.m.	26/09/2013 19:00	1012:00:00		**E43**	27.77				26.723	1.168	7.39	5810	203	67.6		900
									1136	1163.77		27.886	1.219						
45	28-Sep	**12:30 a.m.**										27.886	1.219						
45	28-Sep		12:00 a.m. - 12:30 a.m.	28/09/2013 0:30	1041:30:00		**E45**	11.41				27.886	1.219	8.88			161.6		786
									199	210.41		28.097	1.228						
45	28-Sep		10:00 p.m.	28/09/2013 22:00	1063:00:00				1185	1185		29.282	1.280						
48	1-Oct	**7:15 p.m.**										29.282	1.280						
48	1-Oct		7:30 p.m. - 8:00 p.m.	1/10/2013 20:00	1133:00:00		**E48**	29.78				29.282	1.280	7.57	6440	178			962
									0	29.78		29.312	1.281						
49	2-Oct	**2:15 p.m.**										29.312	1.281						
49	2-Oct		2:00 p.m. - 2:15 p.m.	2/10/2013 14:15	1151:15:00		**E49**	60.14				29.312	1.281	7.61	5800		215.2	22.2	817
										60.14		29.372	1.284						
50	3-Oct		10:00 p.m.	3/10/2013 22:00	1183:00:00					0		29.372	1.284						
50	3-Oct	**10:00 p.m.**										29.372	1.284						
51	4-Oct		4:00 p.m. - 4:30 p.m.	4/10/2013 16:30	1201:30:00	19.87	**E51**	23.65				29.372	1.284	8.02	5600		178.4		827
									334	357.65		29.729	1.299						
52	5-Oct		6:00 p.m.	5/10/2013 18:00	1227:00:00				429	429		30.158	1.318						
52	5-Oct	**6:00 p.m.**										30.158	1.318						
54	7-Oct		6:00 p.m. - 6:30 p.m.	7/10/2013 18:30	1275:30:00		**E54**	46.62				30.158	1.318	7.67	6080	175	35.6		984
									1309.5	1356.12		31.514	1.377						
54	7-Oct	**8:30 p.m.**										31.514	1.377						
54	7-Oct		8:00 p.m. - 8:30 p.m.	7/10/2013 20:30	1277:30:00		**E54.1**	27.27				31.514	1.377	8.55	5810		236.4		824
									72.22	99.49		31.614	1.381						
56	9-Oct		6:00 p.m. - 6:30 p.m.	9/10/2013 18:30	1323:30:00				1146.5	1146.5		32.760	1.432						
56	9-Oct	**6:30 p.m.**										32.760	1.432						
58	11-Oct		6:00 p.m. - 6:30 p.m.	11/10/2013 18:30	1371:30:00		**E58**	49.29				32.760	1.432	7.55	6030	121	31.2	67.6	921
									1284	1333.29		34.094	1.490						

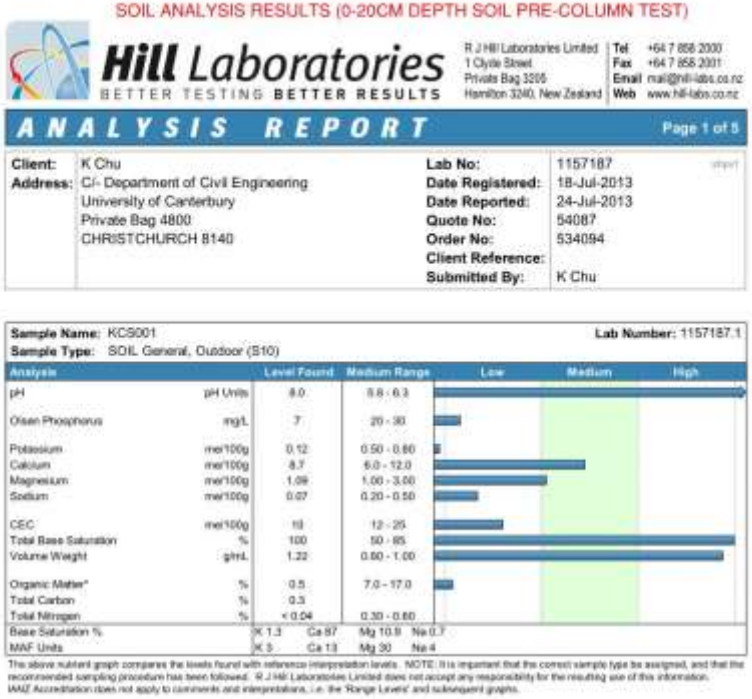
Appendix D 3: control case column experiment data.

										INITIAL DIW VALUES:	8.25	0.9	0	0	0	0
Day	**Date**	**Irrigation Time**	**Leachate Collection Time**	**Time Stamp**	**Cumulative Time, hh:mm:ss**	**Column Flow Rate, ml/hr**	**Code**	**Weight of Analysis Sample Collected, g**	**Pore Volume Weight, g**	**Total Pore Volume, ml**	**pH**	**Conductivity (uS/cm)**	**Total Nitrogen, mg/L**	**Ammonia cal-N, mg/L**	**Nitrate-N, mg/L**	**COD, mg/L**
1	15-Aug	**3:00 p.m.**		15/08/2013 15:00												
1	15-Aug		9:00 p.m. - 9:10 p.m.	15/08/2013 21:10	6:10:00	205.71	**F1.1**	33.26			8.04	411.5	UR	-0.3	4	17
									1201	1234.26						
3	17-Aug		3:00 p.m.	17/08/2013 15:00	48:00:00				82	82						
3	17-Aug	**3:30 p.m.**		17/08/2013 15:30	48:30:00											
3	17-Aug		6:00 p.m. - 6:20 p.m.	17/08/2013 18:20	51:20:00		**F3.1**	44.01			8.09	442.7		-0.2	5.5	2
									655.21	699.22						
			11:00 p.m. - 11:30 p.m.	17/08/2013 23:30	56:30:00	124.632	**F3.2**	11.42			8.28	404		-0.2		20
									611.74	623.16						
4	18-Aug		1:30 a.m.	18/08/2013 1:30	58:30:00				0	0						
5	19-Aug		4:30 p.m.	19/08/2013 16:30	97:30:00				0	0						
5	19-Aug	**4:30 p.m.**		19/08/2013 16:30	97:30:00											
5	19-Aug		8:00 p.m. - 8:20 p.m.	19/08/2013 20:20	101:20:00		**F5.1**	55.56			8.1	435.3		0.1	6.5	5
									1141.34	1196.9						
7	21-Aug		10:00 a.m.	21/08/2013 10:00	139:00:00				132.72	132.72						
7	21-Aug	**10:00 a.m.**		21/08/2013 10:00	139:00:00											
7	21-Aug		1:50 p.m. - 2:00 p.m.	21/08/2013 14:00	143:00:00	261.02	**F7.1**	30.08			8.23	438.2	UR	0.2	3	45
									1014	1044.08						
8	22-Aug		11:30 p.m.	22/08/2013 23:30	176:30:00				251.31	251.31						
9	23-Aug	**6:30 p.m.**		23/08/2013 18:30	195:30:00											
10	24-Aug		2:30 a.m. - 2:50 a.m.	24/08/2013 2:50	203:50:00	144.8517647	**F10.1**	2.45						UR		
									1228.79	1231.24						
11	25-Aug		3:30 p.m.	25/08/2013 15:30	240:30:00				0	0						
11	25-Aug	**3:30 p.m.**		25/08/2013 15:30	240:30:00											
11	25-Aug		8:30 p.m. - 8:50 p.m.	25/08/2013 20:50	245:50:00	239.0363636	**F11.1**	27.75			8.21	423		0	9.5	12
									1286.95	1314.7						
12	26-Aug		1:00 a.m. - 1:30 a.m.	26/08/2013 1:30	250:30:00		**F12.1**	8.91			8.1			0.1	4.5	4
									30.13	39.04						
13	27-Aug		1:30 a.m.	27/08/2013 1:30	274:30:00				0	0						
13	27-Aug	**2:30 p.m.**		27/08/2013 14:30	287:30:00											
13	27-Aug		8:00 p.m. - 8:30 p.m.	27/08/2013 20:30	293:30:00	234.055	**F13.1**	22.15			8.2	434.6	UR	-0.3	2	2
									1382.18	1404.33						
14	28-Aug		10:00 p.m.	28/08/2013 22:00	319:00:00				0	0						
15	29-Aug	**3:00 p.m.**														
15	29-Aug		7:30 p.m. - 8:00 p.m.	29/08/2013 20:30	341:30:00		**F15.1**	22.84			>>	>>	>>	>>	>>	>>
									1518.71	1541.55						
17	31-Aug		7:00 p.m.	31/08/2013 19:00	388:00:00				0	0						

Appendix D 4: KBr column experiment data.

Day	Date	Irrigation Time	Leachate Collection Time	Time Stamp	Cumulative Time (hh:mm:ss)	Column Flow Rate (ml/hr)	Code	Weight of Analysis Sample Collected, g	Pore Volume Weight, g	Total Pore Volume, ml	Cumulative pore volume, Liters	Pore volume, unitless	Total Bromine, mg/L
1	21-Oct	**3:00 p.m.**											
1	21-Oct		7:00 p.m.	21/10/2013 15:00	0:00:00		**B1**	45.76	726.24	772	0.772	0.033735377	65
4	24-Oct	**6:40 p.m.**										0	
4	24-Oct		7:20:00 p.m. - 7:25:00 p.m.	24/10/2013 19:20	76:20:00		**B4**	32.36	921	953.36	1.72536	0.075395945	90
4	24-Oct		8:30 p.m.	24/10/2013 20:30	77:30:00				145	145	1.87036	0.081732253	
6	26-Oct	**6:40 p.m.**									1.87036	0.081732253	
6	26-Oct		7:30:00 p.m. - 7:35:00 p.m.	26/10/2013 19:35	124:35:00		**B6**	55.73	851.66	907.39	2.77775	0.121383994	111
8	28-Oct		8:00 p.m.	28/10/2013 20:00	173:00:00				183	183	2.96075	0.129380851	
8	28-Oct	**8:00 p.m.**									2.96075	0.129380851	
8	28-Oct		8:15:00 p.m. - 8:20:00 p.m.	28/10/2013 20:20	173:20:00		**B8**	59.95	248	307.95	3.2687	0.142837858	110
11	31-Oct	**6:00 p.m.**									3.2687	0.142837858	
11	31-Oct		5:50 p.m.	31/10/2013 17:50	242:50:00				855.16	855.16	4.12386	0.180207217	
11	31-Oct		6:05:00 p.m. - 6:10:00 p.m.	31/10/2013 18:10	243:10:00		**B11**	27.86	566	593.86	4.71772	0.206158112	132
15	4-Nov	**8:00 p.m.**									4.71772	0.206158112	
15	4-Nov		8:00:00 p.m. - 8:05:00 p.m.	4/11/2013 20:05	341:05:00		**B15**	56.56	573	629.56	5.34728	0.233669049	95
18	7-Nov	**6:30 p.m.**									5.34728	0.233669049	
18	7-Nov		6:30:00 p.m. - 6:35:00 p.m.	7/11/2013 18:35	411:35:00		**B18**	29.02	1069	1098.02	6.4453	0.281651068	142
20	9-Nov	**10:00 p.m.**									6.4453	0.281651068	
20	9-Nov		10:00:00 p.m. - 10:05:00 p.m.	9/11/2013 22:05	463:05:00		**B20**	34.02	1181	1215.02	7.66032	0.334745832	151
22	11-Nov	**10:00 p.m.**									7.66032	0.334745832	
22	11-Nov		7:00:00 p.m. - 7:05:00 p.m.	11/11/2013 19:05	508:05:00		**B22**	54.84	1215	1269.84	8.93016	0.390236157	159
24	13-Nov	**7:00 p.m.**									8.93016	0.390236157	
24	13-Nov		7:00:00 p.m. - 7:05:00 p.m.	13/11/2013 19:05	556:05:00		**B24**	29.37	1199	1228.37	10.15853	0.443914298	157
26	15-Nov	**7:30 p.m.**									10.15853	0.443914298	
26	15-Nov		7:30:00 p.m. - 7:35:00 p.m.	15/11/2013 19:35	604:35:00		**B26**	15.3	1087	1102.3	11.26083	0.492083347	177

Appendix E: External laboratory sampling data



SOIL ANALYSIS RESULTS (0-20CM DEPTH SOIL PRE-COLUMN TEST)

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ANALYSIS REPORT

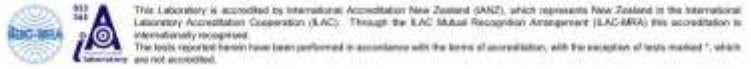
Page 1 of 5

Client:	K Chu	Lab No:	1157187
Address:	C/- Department of Civil Engineering	Date Registered:	18-Jul-2013
	University of Canterbury	Date Reported:	24-Jul-2013
	Private Bag 4800	Quote No:	54087
	CHRISTCHURCH 8140	Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

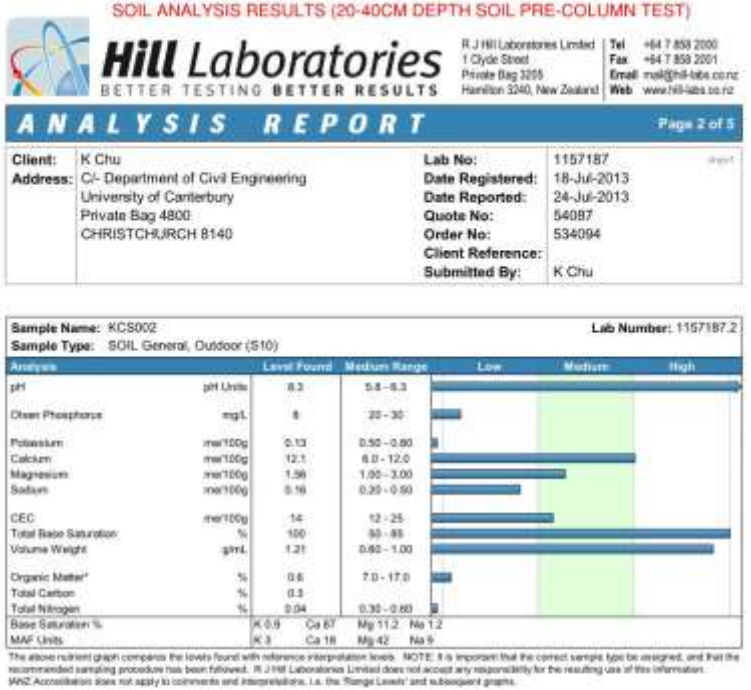
Sample Name: KCS001 — Lab Number: 1157187.1
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low	Medium	High
pH	pH Units	8.0	5.8 - 6.3			
Olsen Phosphorus	mg/L	7	20 - 30			
Potassium	me/100g	0.12	0.50 - 0.80			
Calcium	me/100g	8.7	6.0 - 12.0			
Magnesium	me/100g	1.09	1.00 - 3.00			
Sodium	me/100g	0.07	0.20 - 0.50			
CEC	me/100g	10	12 - 25			
Total Base Saturation	%	100	50 - 85			
Volume Weight	g/mL	1.22	0.60 - 1.00			
Organic Matter*	%	0.5	7.0 - 17.0			
Total Carbon	%	0.3				
Total Nitrogen	%	< 0.04	0.30 - 0.60			
Base Saturation %		K 1.3	Ca 87	Mg 10.9	Na 0.7	
MAF Units		K 3	Ca 13	Mg 30	Na 4	

This above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information. IANZ Accreditation does not apply to comments and interpretations, i.e. the 'Range Levels' and subsequent graphs.



This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised.
The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.



SOIL ANALYSIS RESULTS (20-40CM DEPTH SOIL PRE-COLUMN TEST)

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ANALYSIS REPORT

Page 2 of 5

Client:	K Chu	Lab No:	1157187
Address:	C/- Department of Civil Engineering	Date Registered:	18-Jul-2013
	University of Canterbury	Date Reported:	24-Jul-2013
	Private Bag 4800	Quote No:	54087
	CHRISTCHURCH 8140	Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

Sample Name: KCS002 — Lab Number: 1157187.2
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low	Medium	High
pH	pH Units	8.3	5.8 - 6.3			
Olsen Phosphorus	mg/L	8	20 - 30			
Potassium	me/100g	0.13	0.50 - 0.80			
Calcium	me/100g	12.1	6.0 - 12.0			
Magnesium	me/100g	1.56	1.00 - 3.00			
Sodium	me/100g	0.16	0.20 - 0.50			
CEC	me/100g	14	12 - 25			
Total Base Saturation	%	100	50 - 85			
Volume Weight	g/mL	1.21	0.60 - 1.00			
Organic Matter*	%	0.6	7.0 - 17.0			
Total Carbon	%	0.3				
Total Nitrogen	%	0.04	0.30 - 0.60			
Base Saturation %		K 0.9	Ca 67	Mg 11.2	Na 1.2	
MAF Units		K 3	Ca 18	Mg 42	Na 9	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information. IANZ Accreditation does not apply to comments and interpretations, i.e. the 'Range Levels' and subsequent graphs.

SOIL ANALYSIS RESULTS (40-60CM DEPTH SOIL PRE-COLUMN TEST)

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ANALYSIS REPORT

Client:	K Chu	**Lab No:**	1157187
Address:	C/- Department of Civil Engineering University of Canterbury Private Bag 4800 CHRISTCHURCH 8140	**Date Registered:**	18-Jul-2013
		Date Reported:	24-Jul-2013
		Quote No:	54087
		Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

Sample Name: KCS003 **Lab Number:** 1157187.3
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	8.3	5.8 - 6.3	
Olsen Phosphorus	mg/L	9	20 - 30	
Potassium	me/100g	0.12	0.50 - 0.80	
Calcium	me/100g	11.7	6.0 - 12.0	
Magnesium	me/100g	1.42	1.00 - 3.00	
Sodium	me/100g	0.20	0.20 - 0.50	
CEC	me/100g	13	12 - 25	
Total Base Saturation	%	100	80 - 85	
Volume Weight	g/mL	1.23	0.60 - 1.00	
Organic Matter*	%	0.5	7.0 - 17.0	
Total Carbon	%	0.3		
Total Nitrogen	%	< 0.04	0.30 - 0.60	
Base Saturation %		K 0.9 Ca 87	Mg 10.8 Na 1.5	
MAF Units		K 3 Ca 16	Mg 39 Na 11	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information. IANZ Accreditation does not apply to comments and interpretations, i.e. the "Range Levels" and subsequent graphs.

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ANALYSIS REPORT

Client:	K Chu	**Lab No:**	1157187
Address:	C/- Department of Civil Engineering University of Canterbury Private Bag 4800 CHRISTCHURCH 8140	**Date Registered:**	18-Jul-2013
		Date Reported:	24-Jul-2013
		Quote No:	54087
		Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

Analyst's Comments

Samples 1-3 Comment:
The medium range guidelines shown in the histogram report relate to sampling protocols as per Hill Laboratories' crop guides and are based on reference values where these are published. Results for samples collected to different depths than those described in the crop guide should be interpreted with caution.
For pastoral soils, the medium ranges are specific for a 75mm sample depth, but if a 150mm sampling depth is used the nutrient levels measured may appear low against these ranges, as nutrients are typically more concentrated in the top of the soil profile. These soil profile differences are altered upon cultivation or contouring.

Sample 1 Comment:
The low CEC level found in this soil indicates that it can only retain cation nutrients (potassium, calcium, magnesium and sodium) at low levels. The normal ranges and the derived histograms are based on a typical soil with a CEC level between 12 and 25 me/100g. The % base saturation data for each element provides an alternative presentation that may be more appropriate for soils with atypical CEC values. Normal %BS levels, as a general guide, are: K 2%-5%, Ca 50%-75%, Mg 5%-15%, Na 1%-2%.

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Soil

Test	Method Description	Default Detection Limit	Samples
Sample Registration*	Samples were registered according to instructions received.	-	1-3
Soil Prep (Dry & Grind)*	Air dried at 35 - 40°C overnight (residual moisture typically 4%) and crushed to pass through a 2mm screen.	-	1-3
pH	1:2 (v/v) soil water slurry followed by potentiometric determination of pH.	0.1 pH Units	1-3
Olsen Phosphorus	Olsen extraction followed by Molybdenum Blue colorimetry.	1 mg/L	1-3
Potassium (MAF)	1M Neutral ammonium acetate extraction followed by ICP-OES.	1 MAF units	1-3
Calcium (MAF)	1M Neutral ammonium acetate extraction followed by ICP-OES.	1 MAF units	1-3
Magnesium (MAF)	1M Neutral ammonium acetate extraction followed by ICP-OES.	1 MAF units	1-3
Sodium (MAF)	1M Neutral ammonium acetate extraction followed by ICP-OES.	2 MAF units	1-3
Organic Matter*	Organic Matter is 1.72 x Total Carbon.	0.2 %	1-3
Total Carbon	Dumas combustion.	0.1 %	1-3
Total Nitrogen	Dumas combustion.	0.04 %	1-3
Potassium	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.01 me/100g	1-3
Calcium	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.5 me/100g	1-3
Magnesium	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.04 me/100g	1-3
Sodium	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.05 me/100g	1-3
Potassium (Sat)	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.1 %BS	1-3
Calcium (Sat)	1M Neutral ammonium acetate extraction followed by ICP-OES.	1 %BS	1-3
Magnesium (Sat)	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.2 %BS	1-3
Sodium (Sat)	1M Neutral ammonium acetate extraction followed by ICP-OES.	0.1 %BS	1-3
CEC	Summation of extractable cations (K, Ca, Mg, Na) and extractable acidity.	2 me/100g	1-3

SOIL ANALYSIS RESULTS (COLUMN E 10-25CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

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ANALYSIS REPORT

Client:	K Chu	**Lab No:**	1157187
Address:	C/- Department of Civil Engineering University of Canterbury Private Bag 4800 CHRISTCHURCH 8140	**Date Registered:**	18-Jul-2013
		Date Reported:	24-Jul-2013
		Quote No:	54087
		Order No:	534094
		Client Reference:	
		Submitted By:	K Chu

Sample Type: Soil

Test	Method Description	Default Detection Limit	Samples
Total Base Saturation	Calculated from Extractable Cations and Cation Exchange Capacity	0 %	1-3
Volume Weight	The weight/volume ratio of dried, ground soil	0.01 g/mL	1-3

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Wendy Homewood
Operations Support - Agriculture Division

Hill Laboratories
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ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury Private Bag 4800 CHRISTCHURCH 8140	**Date Registered:**	19-Oct-2013
		Date Reported:	24-Oct-2013
		Quote No:	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col E - 1025 **Lab Number:** 1193584.1
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	8.5	5.8 - 6.3	
Olsen Phosphorus	mg/L	8	20 - 30	
Potassium	me/100g	0.79	0.50 - 0.80	
Calcium	me/100g	7.0	6.0 - 12.0	
Magnesium	me/100g	0.64	1.00 - 3.00	
Sodium	me/100g	1.41	0.20 - 0.50	
CEC	me/100g	10	12 - 25	
Total Base Saturation	%	100	50 - 85	
Volume Weight	g/mL	1.28	0.60 - 1.00	
Organic Matter*	%	0.4	7.0 - 17.0	
Total Carbon	%	0.2		
Total Nitrogen	%	0.07	0.30 - 0.60	
Base Saturation %		K 8.1 Ca 71	Mg 6.5 Na 14.4	
MAF Units		K 21 Ca 11	Mg 18 Na 83	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information. IANZ Accreditation does not apply to comments and interpretations, i.e. the 'Range Levels' and subsequent graphs.

This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised.
The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

SOIL ANALYSIS RESULTS (COLUMN E 0-10CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

Hill Laboratories
BETTER TESTING BETTER RESULTS
R J Hill Laboratories Limited | Tel +64 7 858 2000
1 Clyde Street | Fax +64 7 858 2001
Private Bag 3205 | Email mail@hill-labs.co.nz
Hamilton 3240, New Zealand | Web www.hill-labs.co.nz

ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury	**Date Registered:**	19-Oct-2013
	Private Bag 4800	**Date Reported:**	24-Oct-2013
	CHRISTCHURCH 8140	**Quote No:**	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col E - 0010 **Lab Number:** 1193584.2
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	8.7	5.8 - 6.3	
Olsen Phosphorus	mg/L	10	20 - 30	
Potassium	me/100g	0.86	0.50 - 0.80	
Calcium	me/100g	5.5	6.0 - 12.0	
Magnesium	me/100g	0.88	1.00 - 3.00	
Sodium	me/100g	1.40	0.20 - 0.50	
CEC	me/100g	9	12 - 25	
Total Base Saturation	%	100	50 - 85	
Volume Weight	g/mL	1.22	0.60 - 1.00	
Organic Matter*	%	0.7	7.0 - 17.0	
Total Carbon	%	0.4		
Total Nitrogen	%	0.07	0.30 - 0.60	
Base Saturation %		K 9.9 Ca 64	Mg 10.2 Na 16.3	
MAF Units		K 21 Ca 8	Mg 24 Na 78	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information.
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SOIL ANALYSIS RESULTS (COLUMN E 25-40CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

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ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury	**Date Registered:**	19-Oct-2013
	Private Bag 4800	**Date Reported:**	24-Oct-2013
	CHRISTCHURCH 8140	**Quote No:**	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col E - 2540 **Lab Number:** 1193584.3
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	8.4	5.8 - 6.3	
Olsen Phosphorus	mg/L	6	20 - 30	
Potassium	me/100g	0.59	0.50 - 0.80	
Calcium	me/100g	5.2	6.0 - 12.0	
Magnesium	me/100g	0.57	1.00 - 3.00	
Sodium	me/100g	1.34	0.20 - 0.50	
CEC	me/100g	8	12 - 25	
Total Base Saturation	%	100	50 - 85	
Volume Weight	g/mL	1.30	0.60 - 1.00	
Organic Matter*	%	0.6	7.0 - 17.0	
Total Carbon	%	0.4		
Total Nitrogen	%	0.06	0.30 - 0.60	
Base Saturation %		K 7.6 Ca 68	Mg 7.4 Na 17.4	
MAF Units		K 16 Ca 8	Mg 17 Na 80	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information.
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SOIL ANALYSIS RESULTS (COLUMN D 25-40CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

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ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury	**Date Registered:**	19-Oct-2013
	Private Bag 4800	**Date Reported:**	24-Oct-2013
	CHRISTCHURCH 8140	**Quote No:**	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col D - 2540 **Lab Number:** 1193584.4
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	8.1	5.8 - 6.3	
Olsen Phosphorus	mg/L	7	20 - 30	
Potassium	me/100g	0.16	0.50 - 0.80	
Calcium	me/100g	10.7	6.0 - 12.0	
Magnesium	me/100g	1.05	1.00 - 3.00	
Sodium	me/100g	0.42	0.20 - 0.50	
CEC	me/100g	12	12 - 25	
Total Base Saturation	%	100	50 - 85	
Volume Weight	g/mL	1.25	0.60 - 1.00	
Organic Matter*	%	0.4	7.0 - 17.0	
Total Carbon	%	0.2		
Total Nitrogen	%	< 0.04	0.30 - 0.60	
Base Saturation %		K 1.3 Ca 87	Mg 8.6 Na 3.4	
MAF Units		K 4 Ca 17	Mg 30 Na 24	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information.
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SOIL ANALYSIS RESULTS (COLUMN D 10-25CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

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ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury	**Date Registered:**	19-Oct-2013
	Private Bag 4800	**Date Reported:**	24-Oct-2013
	CHRISTCHURCH 8140	**Quote No:**	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col D - 1025 **Lab Number:** 1193584.5
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range	Low / Medium / High
pH	pH Units	7.8	5.8 - 6.3	
Olsen Phosphorus	mg/L	6	20 - 30	
Potassium	me/100g	0.11	0.50 - 0.80	
Calcium	me/100g	7.7	6.0 - 12.0	
Magnesium	me/100g	0.82	1.00 - 3.00	
Sodium	me/100g	0.36	0.20 - 0.50	
CEC	me/100g	9	12 - 25	
Total Base Saturation	%	100	50 - 85	
Volume Weight	g/mL	1.34	0.60 - 1.00	
Organic Matter*	%	0.4	7.0 - 17.0	
Total Carbon	%	0.2		
Total Nitrogen	%	< 0.04	0.30 - 0.60	
Base Saturation %		K 1.3 Ca 86	Mg 9.1 Na 4.0	
MAF Units		K 3 Ca 13	Mg 25 Na 22	

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information.
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SOIL ANALYSIS RESULTS (COLUMN D 0-10CM SOIL, POST-IRRIGATION SOIL ANALYSIS)

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ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1193584
Address:	University of Canterbury	**Date Registered:**	19-Oct-2013
	Private Bag 4800	**Date Reported:**	24-Oct-2013
	CHRISTCHURCH 8140	**Quote No:**	54087
		Order No:	537174
		Client Reference:	
		Submitted By:	P McGuigan

Sample Name: Col D - 0010 **Lab Number:** 1193584.6
Sample Type: SOIL General, Outdoor (S10)

Analysis		Level Found	Medium Range
pH	pH Units	7.6	5.8 - 6.3
Olsen Phosphorus	mg/L	7	20 - 30
Potassium	me/100g	0.18	0.50 - 0.80
Calcium	me/100g	7.6	6.0 - 12.0
Magnesium	me/100g	0.79	1.00 - 3.00
Sodium	me/100g	0.37	0.20 - 0.50
CEC	me/100g	9	12 - 25
Total Base Saturation	%	100	50 - 85
Volume Weight	g/mL	1.31	0.60 - 1.00
Organic Matter*	%	0.5	7.0 - 17.0
Total Carbon	%	0.3	
Total Nitrogen	%	0.05	0.30 - 0.60
Base Saturation %		K 2.0 Ca 85	Mg 8.8 Na 4.2
MAF Units		K 5 Ca 12	Mg 23 Na 22

The above nutrient graph compares the levels found with reference interpretation levels. NOTE: It is important that the correct sample type be assigned, and that the recommended sampling procedure has been followed. R J Hill Laboratories Limited does not accept any responsibility for the resulting use of this information. IANZ Accreditation does not apply to comments and interpretations, i.e. the 'Range Levels' and subsequent graphs.